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THE CONSTITUTION OF MATTER

THE CONSTITUTION OF MATTER

MODERN ATOMIC AND ELECTRON THEORIES

BY

MAX BORN

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TRANSLATED FROM THE SECOND REVISED GERMAN EDITION BY

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TRANSLATORS' PREFACE

THIS translation is from the second revised German edition; it is hoped that it is not too literal a rendering of the original, our object being to produce a readable and accurate version.

The current German edition has been specially amplified for this translation by the author, to whom our thanks are due, and we are also deeply indebted to Mr. W. G. King for his invaluable help in the translation.

E. W. B.
T. S. W.

April, 1923

PREFACE TO THE FIRST EDITION

THE three essays which form the contents of this little book have appeared during the past year in "Die Naturwissenschaften." They deal with the one subject, the physical theory of atoms, from different points of view; the first gives a general survey of the modern theory of atoms, whilst the other two discuss questions which I myself have endeavoured to answer. The similarity of subject matter involves several repetitions,

but to condense the three essays into one comprehensive summary seemed to me impossible without detriment to their character. It would also be out of place, since A. Sommerfeld has recently published a book, "Atomic Structure and Spectral Lines," translated by H. L. Brose (Methuen & Co. Ltd.), which deals comprehensively, yet simply, with the recent advances in the physical atomic theory. These essays are for those who have not time to study the larger work of Sommerfeld.

M. BORN

FRANKFURT A. M., *20th April, 1920*

PREFACE TO THE SECOND EDITION

THE form of these essays precludes any extensive alterations. I have therefore had to confine myself to incorporating the most important of the recent advances, particularly Aston's work on isotopy in ordinary elements, Franck's spectroscopic determination of the electron-affinities of halogen atoms, and Knipping's measurements of the ionisation-energies of the hydrogen halides. For the rest I have only made minor alterations and additions to the references. Dr. R. Minkowski has kindly assisted me in reading the proofs.

M. BORN

GÖTTINGEN, *5th December, 1921*

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THE CONSTITUTION OF MATTER

THE ATOM *

INTRODUCTION

THE modern theory of the atom has its origin in chemistry. Physicists have turned only slowly and reluctantly to the atomic point of view, and while atoms and molecules have long been in daily use by the chemist, it is but a short time since there were physicists who regarded the atomic theory as a sometimes seemingly useful, but in the main avoidable, hypothesis. It is not so to-day. The physicist, helped by the investigations of the last few years, may now presume to instruct the chemist in the nature and the actions of the atom. For physical methods penetrate deeper into the atom than do chemical; while the speculations of chemists on the structure of atoms and the forces at work between them, especially as regards valency, were somewhat arbitrary, being chiefly based on one manifestation of atomic force—chemical combination, the idea of the atom as conceived by present-day physicists is, in many vital respects, free from such arbitrariness. One can be confident that future investigation will amplify, but at the same time leave, the clear outline that we now know.

* From an address delivered on the fiftieth anniversary of the Frankfurter chemischen Gesellschaft, November 1st, 1919.

But what is this outline like ? The space at our disposal is insufficient to show how it gradually grew, like a mosaic, from countless small pieces; it is better, therefore, to describe how modern physics regards the atom, and then deduce some of its properties, which are already empirically known.

This process might be called a synthesis of the universe ; for all matter consists of atoms, so that the physicist can say, like Archimedes : " Give me the atom, and I will build the world."

1. Electrons and Nuclei

In chemistry the atom is still the " smallest," indivisible as its name implies. In physics this can no longer be, for otherwise the question of the constitution of the atom would be meaningless. The innumerable lines of an iron spectrum prove that there must be within an iron atom highly complex oscillations, compared with which those of modern orchestral music are very simple.

The atom being a structure, what are its components ?

First, it will be shown how physics answers this question, and then, as far as space permits, the evidence for the statements will be given.

There are two kinds of components which are distinguished by their electrical charges. *The negatively-charged particles* are all of the same size and equally charged ; they are called *electrons*. Their mass is exceedingly small, about 1/1833, when compared with that of the H atom. It is very probable that *the positively-charged particles* can be referred to a single constituent. This question as it stands to-day will be discussed later ; in the meantime, it may be assumed that there are as many kinds of these positively-charged particles as there are chemical elements. They contain the bulk of the weight and the mass of the atoms, and are therefore called *atom-nuclei*, or simply *nuclei*.

2. The Structure of the Atom

An atom, or ion, consists of one nucleus and a number, z, of electrons. If the atom is "neutral," the charge of the nucleus must be equal to that of the combined electrons, and, as all these are equal and have the same charge, e, the nuclear charge must be a simple multiple of e, namely, ze. The number z is called the *nuclear charge-number, atomic-number,* or *position-number.* One can arrange all the nuclei in a series with increasing values of z, and one then obtains the same order as in the well-known periodic system of the elements (Fig. 1), e.g. H has $z = 1$, He $z = 2$, and so on. It is the nuclear charge that is important, not the atomic weight, for several elements are known where the order in the periodic system, depending on chemical properties, is not that of increasing atomic weight; thus the lighter potassium, K, follows the heavier argon, A, and the lighter nickel, Ni, the heavier cobalt, Co. Later it will be shown that the order of the periodic system is intimately connected with the structure of the atom.

In a neutral atom each nucleus is surrounded by as many electrons as its number z indicates; the H nucleus has one electron, the He nucleus has two electrons, and so on. If one electron is lacking, then the positive nuclear charge is in excess, and a monovalent *positive ion* results. If $z + 1$ electrons are present, then the *ion* is *monovalent* and *negative.* In the same way di- and poly-valent positive and negative ions can be explained. Thus, for instance, the H^+ ion is nothing more than the H nucleus, and the He^{++} ion is the He nucleus, which we shall find again in the α-rays.

3. The Atomic Theory of Electricity

Before we describe the atomic system in detail, the above statements must be proved. In order to account for the phenomenon of electrolysis, Helmholtz had already put forward the hypothesis that electricity, like matter, was

	O.	I. a	I. b	II. a	II. b	III. a	III. b	IV. a	IV. b	V. a	V. b	VI. a	VI. b	VII. a	VII. b	VIII.		
1 H	2 He	3 Li		4 Be		5 B		6 C			7 N		8 O		9 F			
1·008	4·00	6·94		9·1		10·90		12·00			14·01		16·00		19·00			
—	10 Ne	11 Na		12 Mg		13 Al		14 Si			15 P		16 S		17 Cl			
	20·0	23·00		24·32		27·1		28·3			31·04		32·07		35·46			
—	18 A	19 K		20 Ca		21 Sc		22 Ti		23 V		24 Cr		25 Mn		26 Fe	27 Co	28 Ni
	39·9	39·10		40·07		45·1		48·1		51·0		52·0		54·93		55·84	58·97	58·68
—			29 Cu		30 Zn		31 Ga		32 Ge		33 As		34 Se		35 Br			
			63·57		65·37		69·9		72·5		74·96		79·2		79·92			
—	36 Kr	37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 —		44 Ru	45 Rh	46 Pd
	82·92	85·5		87·6		88·7		90·6		93·5		96·0		—		101·7	102·9	106·7
—			47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I			
			107·88		112·4		114·8		118·7		120·2		127·5		126·92			
—	54 X	55 Cs		56 Ba		57 La		58 Ce	59 Pr	60 Nd	61 —	62 Sm	63 Eu	64 Gd				
	130·2	132·8		137·4		139·0		140·3	140·9	144·3	—	150·4	152·0	157·3				
—								65 Tb	66 Dy	67 Ho	68 Er	69 Tu	70 Yb	71 Lu	72 —			
								159·2	162·5	163·5	167·7	169·4	173·5	175·0	—			
—										73 Ta		74 W		75 —		76 Os	77 Ir	78 Pt
										181·5		184·0		—		190·9	193·1	195·2
—			79 Au		80 Hg		81 Tl		82 Pb		83 Bi		84 Po	85 —				
			197·2		200·6		204·0		207·20		209·0		(210·0)	—				
—	86 Em	87 —		88 Ra		89 Ac		90 Th		91 Pa		92 U						
	222·0	—		226·0		(226)		232·1		(234)		238·2						

FIG. 1.—The periodic system of the elements, including atomic numbers and atomic weights.

atomically constituted, thus explaining the well-known law of Faraday, that chemically equivalent weights always transport the same quantity of electricity. The discovery of the cathode rays, and later of the rays of radioactive substances, rendered possible the proof of the Helmholtz hypothesis. If, for instance, one brings a beam of cathode rays into an electrical field, it is deflected as if it consisted of single, negatively-charged, heavy particles. Fig. 2 shows an evacuated glass vessel with anode A and cathode K ; the cathode rays proceed from the latter and traverse the field between two charged condenser plates, wherein they are deflected. By combining an electrical with a magnetic deviation the velocity and the ratio of charge to mass, e/m,

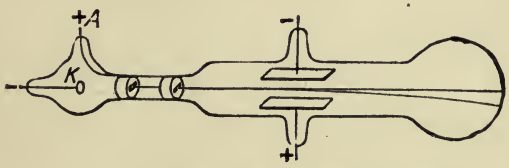


FIG. 2.—Cathode rays in an electrical field.

can be determined.[1] This ratio was found to be many times greater than in electrolysis:

$$\frac{e}{m} = 5{\cdot}31 \times 10^{17} \text{ E.S.U. per gram.}$$

If it be assumed, as is probable, that the charge is the same in both, it follows that the mass of the cathode-ray particles must be much less than that of the atoms, being about 1830 times smaller than that of the H atom. These negative particles are the *electrons*.

4. Positive Electricity

Positive rays have also been found and the ratio e/m determined for them, as, for instance, for the so-called " canal rays " of Goldstein,[2] which travel through holes in the cathode in the direction opposite to that of the cathode

rays and the α-rays of radioactive substances. Here, however, e/m was found to be of the same magnitude as in electrolysis. So far no one has succeeded in isolating positive electricity apart from matter, so that the heavy portions of the atom are these positive elementary particles. Particularly important is the discovery that the α-particles of radioactive substances are doubly-charged He atoms, that is, He nuclei.[3] J. J. Thomson has been able to produce in a vacuum tube canal rays of many elements, and to measure e/m for each of them.[4] The method used has recently been improved by Aston, to whose investigations we will refer later; they throw much light on the nature of the positive elementary particles.

5. The Charge on an Electron

Electrons will now be used to explain numerous electrical and optical phenomena. It has been shown that the colour dispersion of light depends on the vibrations of elastically-bound electrons in the atoms of the dispersing medium, and that the ratio e/m can be calculated from purely optical measurements of the refractive index to agree well with the cathode-ray value.[5] This was accomplished by a study of the way in which the lines of the emission spectra of elements are perturbed and split up in magnetic fields (Zeeman effect).[6]

British physicists studied the conductivity of gases, and explained it by the ionisation of the molecules. These investigations finally led to the discovery of a method of measuring the electrical elementary-quantum, e, in absolute units.[7] Minute drops of water or oil, or metal spheres of microscopic or ultra-microscopic dimensions, become charged in ionised gases, and are deflected in electrical fields, thus forming extremely sensitive electroscopes. In this manner Millikan, of Chicago, found that all charges occurring on the drops were whole multiples of the quantum

$$e = 4{\cdot}77 \times 10^{-10} \text{ E.S.U.}$$

This is now taken to be the charge on the electron. Ehrenhaft, of Vienna, who worked with considerably smaller drops, believed he had detected much smaller charges, and denied the existence of an electron of this magnitude. More recent experiments, particularly those of Regener and his collaborators and of Bär, suggest, however, that the phenomena observed by Ehrenhaft cannot be explained by a subdivision of the elementary charge, but are due rather to the adsorption of gases on the surfaces of the minute spheres, which then appear to possess abnormally small densities.

6. The Magnitude of Electrons and Nuclei

How small must one imagine the electron to be? The answer is given by a universal law of electro-dynamics which is intimately bound up with the modern theory of relativity.

Fig. 3.

By the mass of a body, physics does not understand any particular mass for that quantity of matter, but that which is yielded by its resistance to changes of velocity (acceleration). The masses of two bodies are inversely proportional to the changes of velocity which one and the same force imparts to them. From this definition and the law of the centre of gravity in mechanics, it follows that the mass is not exactly constant, but depends on the energy-content of the body. Einstein has shown this very important fact somewhat as follows:

Imagine a long tube (Fig. 3) at one end of which is a body A, and at the other end a body B, both of exactly the same material and magnitude and therefore, ordinarily speaking, of the same mass. Let A contain a certain amount of energy in excess of B, and also some means whereby this

energy can be radiated in the direction of B in the form of a flash of light. When this occurs, A suffers a recoil through the light-pressure—the existence of which has been proved both experimentally and theoretically—and the whole tube will then move towards the left until the light reaches B and has been absorbed by it. In the collision of the light with B, the light-pressure acts in the opposite direction and with the same force, so that the tube comes to rest in a position slightly removed from the original. Let the two bodies A and B now change places; if they both have the same ordinary mass, and if this alone be mechanically influential, then in the exchange of A and B their centre of gravity will remain at rest, and therefore there will be no change in the position of the tube as a whole. The system is now in its initial condition, except that where A was formerly, B now is, with the same excess of energy, while A itself is in the original state and position of B. Therefore the process can be repeated and the energy radiated from B to A; the tube thereby undergoing a displacement of the same magnitude as before. By sufficient repetition of this process, the body, without the intervention of any exterior force, can be set in motion from rest and transported any given distance. Now this contradicts the fundamental laws of mechanics, and to obviate this anomaly one must assume that, in the exchange of the two bodies A and B, whichever has the excess of energy also has the greater mass, the latter being so balanced that the displacement due to the light-pressure is just neutralised by the subsequent interchange of the bodies.

This increase of mass obviously depends on the excess of energy. It can be shown in other ways that the mass of a body increases with its energy-content, from which it can be seen that the total mass of a body depends on its energy. The exact mathematical analysis on the basis of the principle of relativity yields the law that the mass of a body is

equal to its energy-content divided by the square of the velocity of light:[8]

$$m = \frac{E}{c^2}.$$

If now the electron is no more than an abstract electrical charge, then its energy is proportional to and, choosing the proper units, can be equated to $\frac{e^2}{r}$, where r is the radius of the electron, and the mass, therefore, is

$$m = \frac{e^2}{c^2 r},$$

whence

$$r = \frac{e}{m} \times e \times \frac{1}{c^2}.$$

With the given values of e/m, e and $c = 3 \times 10^{10}$ cms./sec.

$$r = \frac{5{\cdot}3 \times 10^{17} \times 4{\cdot}8 \times 10^{-10}}{9 \times 10^{20}} = 3 \times 10^{-13} \text{ cms.}$$

Reliable estimates of the radii of the atoms are of the magnitude of 10^{-8} cms., therefore the electron is exceedingly small compared with the atom. If one is to imagine the nucleus of the atom as purely electrical, one must think of it as being almost 2000 times heavier than the electron. As our formula shows, mass and radius are inversely proportional, so that the radius of the nucleus is about 2000 times smaller than that of the electron. This remarkable result, that the positively-charged mass is concentrated in an exceedingly minute space, is, as we shall see directly, well supported by experiment.

7. Thomson's Model of the Atom

The nuclei, and the construction of atoms from nuclei and electrons, must now be considered. In order to explain the sharp lines in the spectrum, it had to be assumed that the electrons in the atom could oscillate about a centre of equilibrium with sharply defined vibration periods. But

electrical charges that do not interpenetrate do not form stable configurations. Therefore Lord Kelvin put forward an atomic model, which later was considerably improved by J. J. Thomson.[9] Positive electricity was regarded as a sphere of radius of the order of 10^{-8} cms., in which the negative electrons swim. According to the laws of electrostatics, these will arrange themselves into symmetrical structures, the properties of which have some resemblance to those of the atoms. But in many respects this model fails, more especially in explaining the great number of spectrum lines and the laws which link them together. The Kelvin sphere is also doubtful, owing to its size, which precludes an electrical interpretation of its mass.

8. Rutherford's Nucleus Theory

That that portion of the atom in which its mass is concentrated is small compared with the electron, was first proved by Rutherford and his co-workers,[10] by a study of the dispersion of the α-rays. Figs. 4 and 5, which were obtained by Wilson's method,[11] show the paths of α-particles. These in their passage ionise the air, and when the latter is supersaturated with water vapour, the moisture condenses in minute drops on each ion and renders visible the track of the α-ray. The limited range of the rays can be clearly seen, and it will be observed (Fig. 6) that some of them, towards the end of their paths, suffer sudden sharp deviations. By a careful study of these ranges and dispersions, especially in metal foils, Rutherford ascertained that that portion of matter with which the heavy mass is associated must be exceedingly small to allow the α-rays to penetrate as far as they do, and also to suffer such sudden deviations. From his measurements he also deduced the value of the nuclear charge, and found that, measured in units e, it was equal to half the atomic weight, i.e.:

$$z = \frac{A}{2}.$$

According to this helium would have $z = 4/2 = 2$, and carbon $z = 12/2 = 6$, as shown in Fig. 1. This result was

FIGS. 4 and 5.—Paths of α-rays.

further supported by investigations on the dispersion of X-rays.[12] One can calculate the amount of energy absorbed

by an electron from an electrical wave which, meeting the electron, causes it to vibrate and radiate this energy as dispersed rays into space. Now it may be assumed that each electron of the atom disperses this amount inde-

Fig. 6.—Path of an α-ray showing sudden deflection.

pendently, so that by measurement of the dispersed energy one can obtain a value for z. Again, it is found that

$$z = \frac{A}{2}.$$

9. The Interference of X-rays

That the number z represents the actual number of electrons [13] was first proved by the examination of X-ray spectra, which was made possible by Laue's discovery.[14]

This was based on the assumption that crystals are atom-lattices, having such small lattice-constants that they can be utilised as diffraction-gratings for the short wave-length

X-rays. Fig. 7 shows two such lattices, those for rock-salt, NaCl, and fluorspar, CaF_2.

Fig. 8 shows the Laue apparatus for producing interference

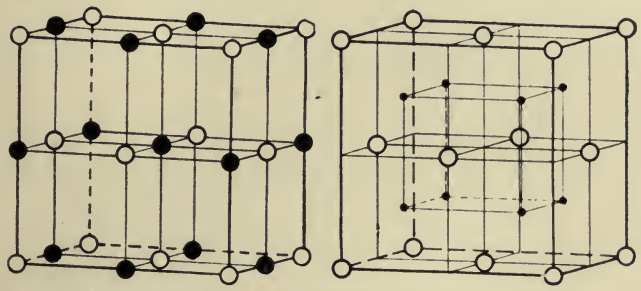


FIG. 7.—Lattice of rock-salt (NaCl) and of fluorspar (CaF_2).

photographs of X-rays. A ray, proceeding from the X-ray tube, meets a crystal K, behind which is placed a photographic plate, P. On this, apart from the image of the direct ray, appear numerous additional spots forming a

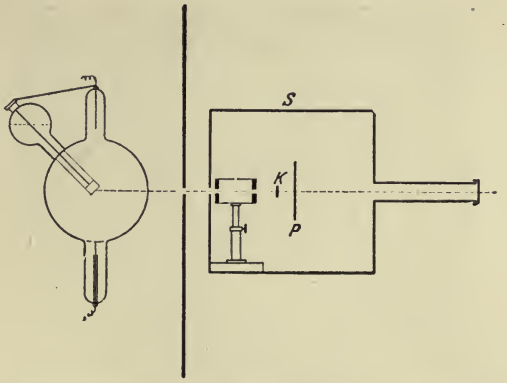
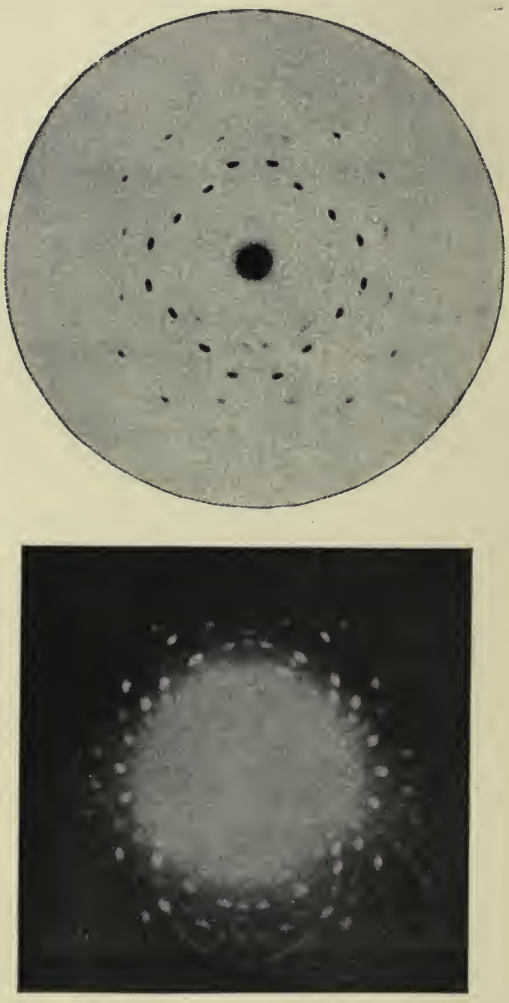


FIG. 8.—Apparatus for producing interference photographs of X-rays (Laue).

distinct pattern, the symmetry of which is directly related to that of the crystal (Figs. 9 and 10). By measurement and calculation from the Laue photographs, one can infer either the structure of the crystal-lattice or the composition (the

" colours ") of the X-rays. Fig. 11 shows, together with the photographs, a theoretical figure in which, by means



FIGS. 9 and 10.—Interference of X-rays (Laue).

of drawn-in lines, the formation and significance of the interference spots is made clear. Sir W. H. Bragg and

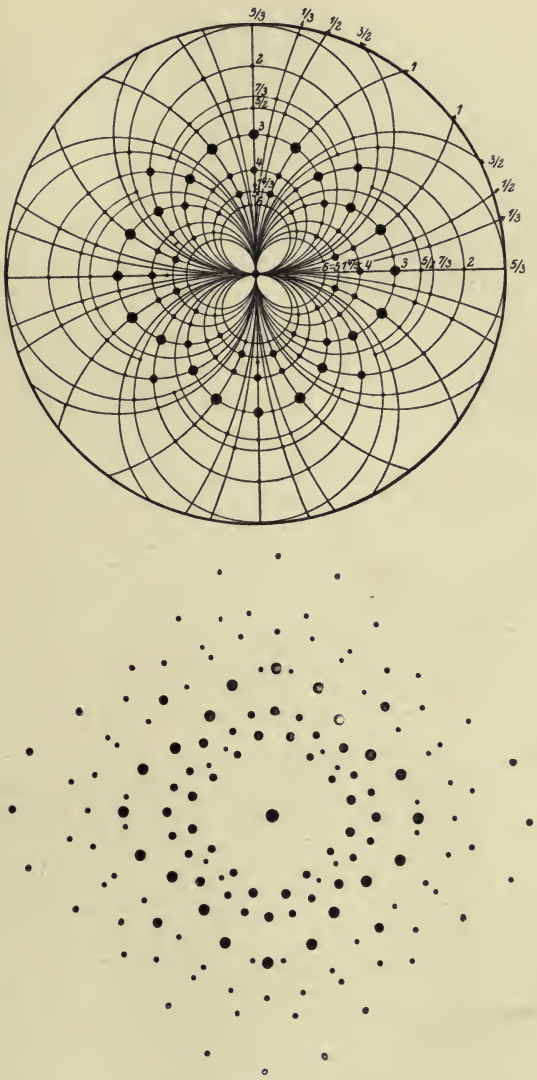


FIG. 11.—Laue interferences and their theoretical explanation.

W. L. Bragg were the first to conduct experiments in X-ray spectroscopy.[15] Using the fact that X-rays are not

reflected at all angles of incidence from a natural crystal, but only at definite angles depending on the wave-length, they rotated the crystal (Fig. 12) in order to obtain successively all possible angles of incidence, and thus produce on the photographic plate "ghosts" of the X-rays. They were the first quantitatively to determine the space-formulæ of simple crystals, and also to measure accurately the wave-lengths of X-rays. The young physicist Moseley, who unfortunately was killed in the war, systematically investigated the X-ray spectra of numerous elements by the Bragg's method.[16] Debye has introduced a modification of their procedure.[17] Instead of rotating a large crystal, he uses a powder of the finest crystals, which set themselves in all possible posi-

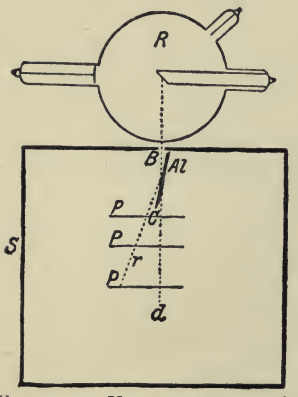


FIG. 12.—X-ray spectrograph (Bragg). *R*, X-ray tube; *B*, diaphragm; *C*, crystal table; *Al*, crystal carrier; *PPP*, photographic plates; *S*, screen; *d*, incident ray; *r*, reflected ray.

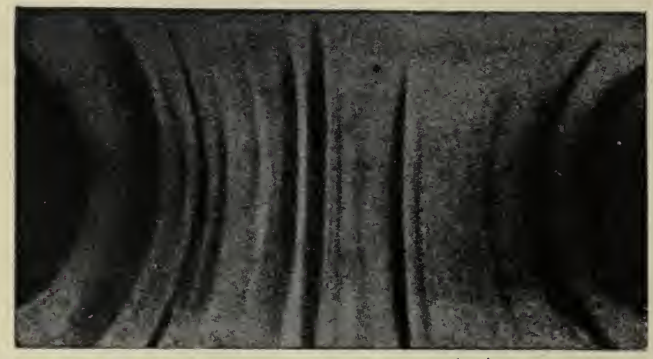


FIG. 13.—X-ray spectrum (Debye).

tions. Fig. 13 is from the original of a photograph of the X-ray spectrum of a metal by this method.

FIG. 14.—X-ray spectrum (Siegbahn).

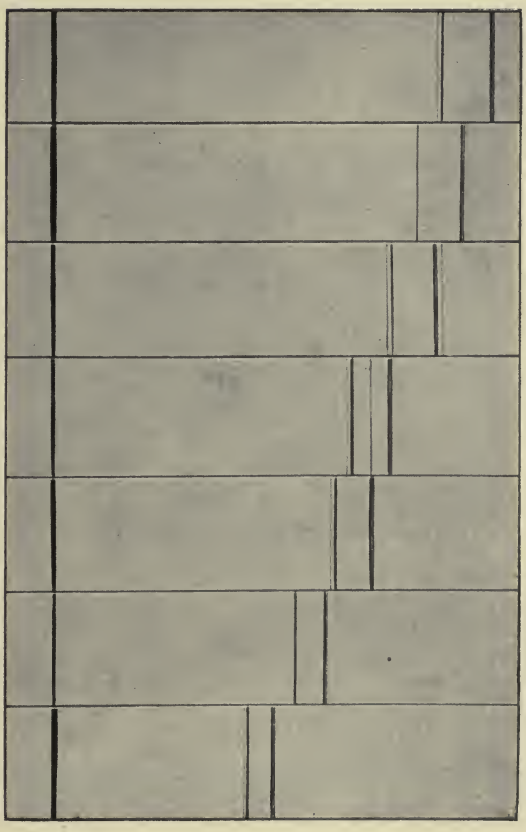


FIG. 15.—The *K*-series for a few elements.

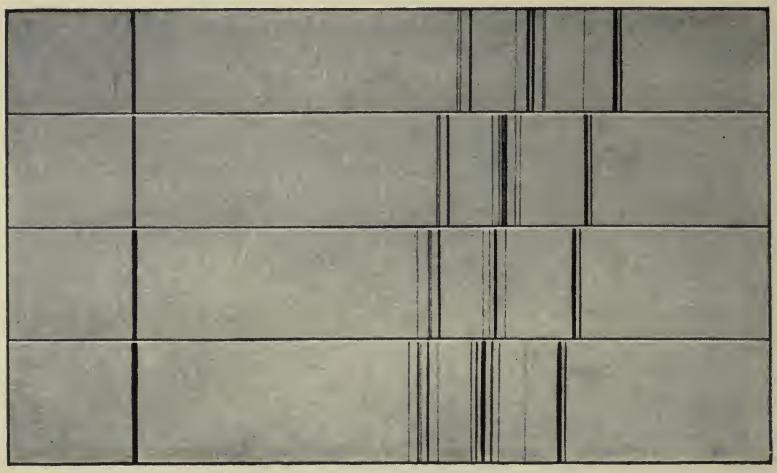


FIG. 16.—The *L*-series for a few elements.

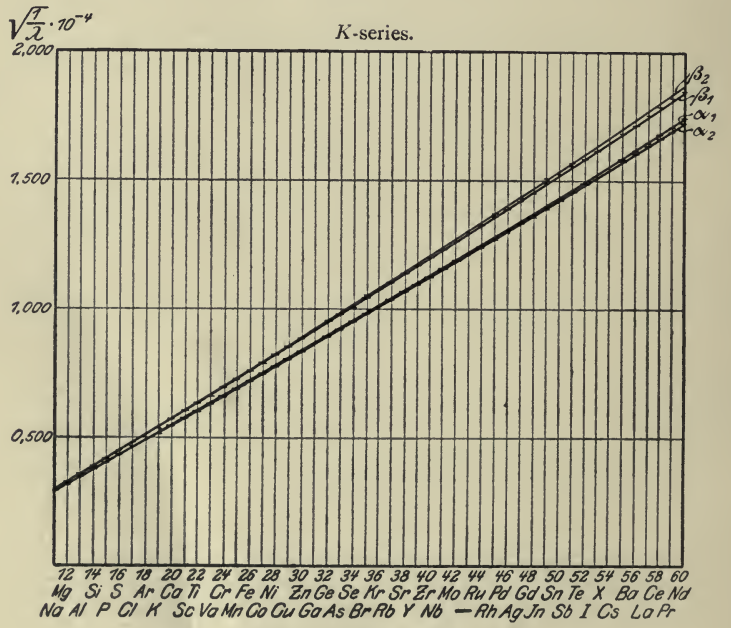

$\sqrt{\frac{\nu}{\lambda}} \cdot 10^{-4}$
K-series.
2,000
1,500
1,000
0,500
β_2
β_1
α_1
α_2
12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60
Mg Si S Ar Ca Ti Cr Fe Ni Zn Ge Se Kr Sr Zr Mo Ru Pd Cd Sn Te X Ba Ce Nd
Na Al P Cl K Sc Va Mn Co Cu Ga As Br Rb Y Nb — Rh Ag Jn Sb I Cs La Pr

FIG. 17.—The *K*-series.

The best exponent of modern X-ray spectroscopy is probably Siegbahn.[18] Fig. 14 is a spectrum photograph taken by him, and shows what a high standard has been attained. The lines in the picture are as clear as those of any optical spectrum.

10. The X-ray Spectra

The main result of these investigations originates, for the most part, from Moseley's work (Figs. 15 and 16).

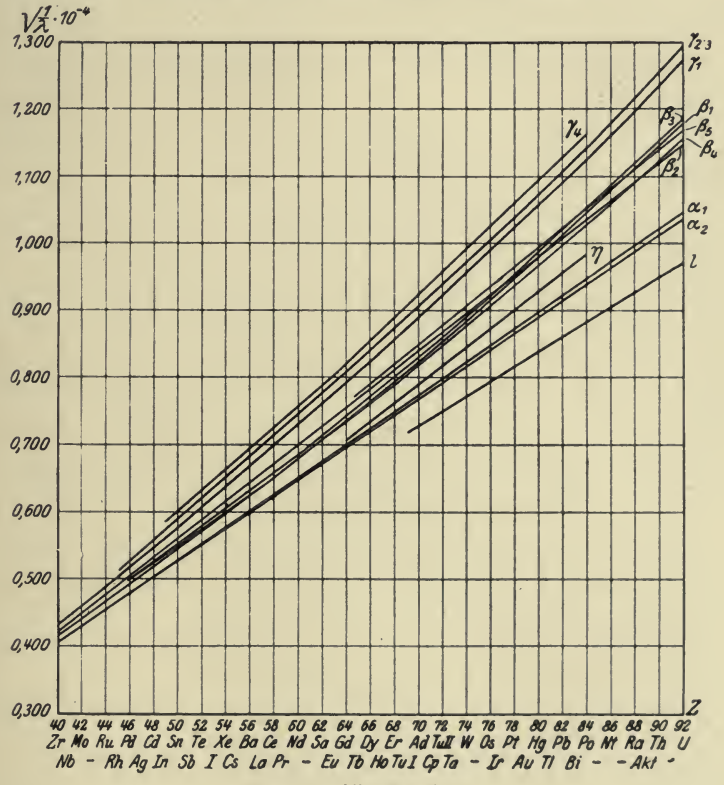


Fig. 18.—The *L*-series.

All elements have, on the whole, the same X-ray spectrum, but all lines shift with increasing atomic number z

towards increasing vibration frequencies ν, or decreasing wave-lengths λ, in such a manner that $\sqrt{\nu}$, or $\frac{1}{\sqrt{\lambda}}$ plotted as a function of z is practically a straight line.[19] Figs. 17 and 18 show the K- and L-series. Each of these series consists of a number of lines, which, plotted from element to element, give an almost straight line. That we really have to deal with the atomic number z, and not with the atomic weight A, is shown in Fig. 19, where $\sqrt{\nu}$ gives, as a function of z, a smooth curve, but, as a function of A, an irregular wavy line.

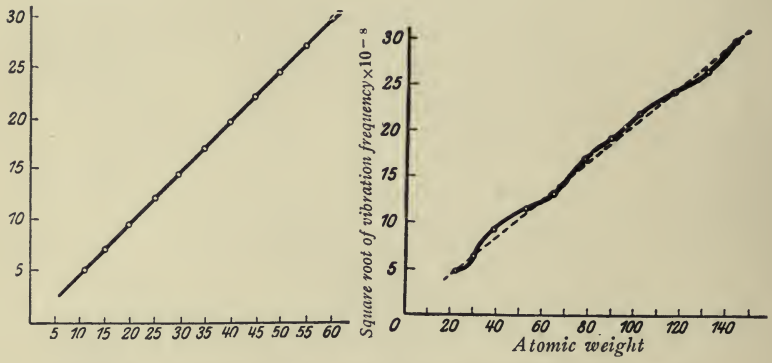


FIG. 19.—The square root of the vibration frequencies in the $K\alpha$-series as a function of the atomic number and of the atomic weight.

This proves the fundamental character of the atomic number z. We now know that argon really comes before potassium and cobalt before nickel; also, that only five elements are missing from the periodic system, for even the rare earths follow the $\sqrt{\nu}$ law. In this way the discovery of the missing elements is facilitated.

11. Atomic Structure

What conclusions concerning the structure of the atom can be drawn from these facts? It is clear that the X-rays originate in the inner part of the atom, whereas its

chemical, optical, and magnetic properties are controlled by the outer structure. Hence the similarity of X-ray spectra proves that:

All atoms have the same internal structure.

This hypothesis, together with the facts that definite X-ray lines first appear at certain elements, and that chemical and physical behaviour is periodic, leads to the idea of a shell-like arrangement of electrons around the nucleus.

The H atom has one electron, the He atom two electrons; these form the first shell, or the first ring. With the alkali metal Li the second shell begins. Consisting at first of one electron, this increases to eight electrons with Ne. Then the third shell commences at Na with one electron, increasing to A, with eight electrons. In the long periods the shell-structure is more complex; this can be seen from the occurrence of families of very similar elements (for instance the iron group Fe, Co, Ni, and the group containing the rare earths). Without going into details two conclusions can be deduced from the above law:

1. The inmost shells of all atoms are, for a certain distance, qualitatively identical, and will therefore produce qualitatively the same X-rays. Quantitatively, however, it is recognised that with increasing nuclear-charge number z the electrons become more closely bound to the nucleus, so that the frequency of the X-rays continuously increases. The quantum theory of emission, to which we will refer later, leads to the law that $\sqrt{\nu}$ is almost proportional to z.

2. The outermost shell has the period 8, and, corresponding with the chemical and optical behaviour, is identical for elements in the same vertical column. Kossel [20] has extended these conceptions qualitatively, and has brought them into agreement with the behaviour of the electro-chemical valencies. He assumes that the configuration of eight electrons,

as shown in the outer shell of the rare gases, is very stable. A shell of one electron is not very stable, the electron is easily detached; two electrons are rather more stable, and so on. A shell of seven electrons seeks to attach another to itself in order to complete a stable configuration of eight;

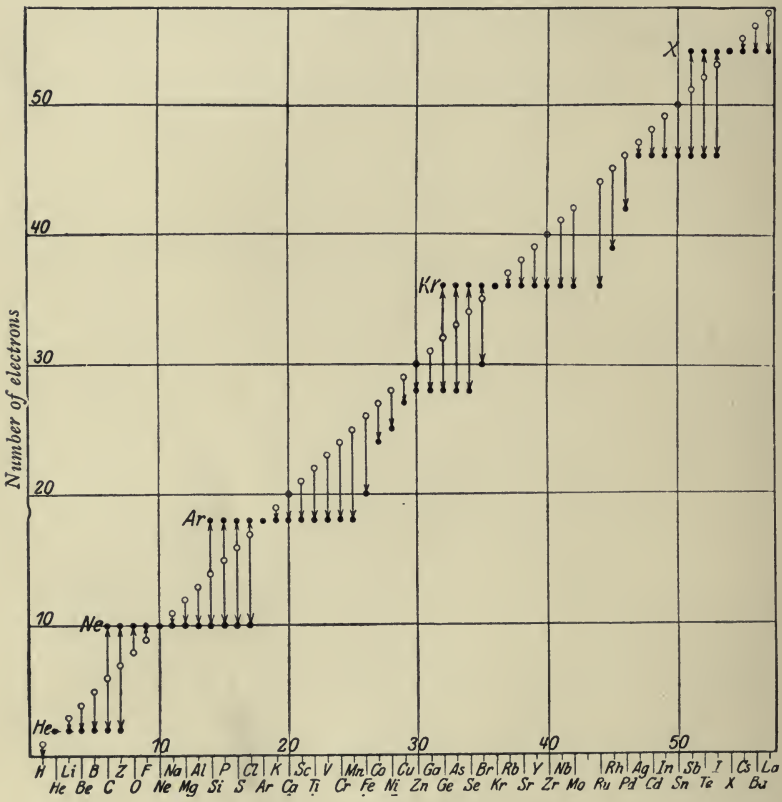

Number of electrons
50
40
30
20
10
He
Ne
Ar
Kr
X
10
20
30
40
50
H Li B Z F Na Al P Cl K Sc V Mn Co Cu Ga As Br Rb Y Nb Rh Ag In Sb I Cs La
He Be C O Ne Mg Si S Ar Ca Ti Cr Fe Ni Zn Ge Se Kr Sr Zr Mo Ru Pd Cd Sn Te X Ba

FIG. 20.—Electro-valencies (Kossel).

a shell of six electrons attracts two, but not so strongly, etc. In this way the polar-valency behaviour becomes clear. Fig. 20 indicates the maximum number of positive and negative electrons that an atom can take up. For example, the number of electrons in a neutral Na atom is eleven

(hollow circle on the diagonal of the illustration) ; it can lose one electron and then move to the horizontal line passing through the rare gas Ne, with ten electrons (black circle).

According to the latest investigations of Bohr,[21] the " shells " should not be regarded as spatially-separate structures enclosing one another; rather is a " shell " a closely bound group of electrons, the centre of which is a definite distance from the nucleus, while each individual electron can at times approach the latter, or recede to a distance from it. To the further development of this idea reference will be made later.

12. Chemical Inferences

In this manner Kossel has explained many chemical facts, especially those relating to complex compounds. What attracts the physicist is that he does this employing only ordinary electrostatic forces, and without postulating particular valencies linking atom to atom like cords or chains. As an example of this method we will consider the formation of the compound NaCl. First, the loose outer electron of the Na atom is detached, and is taken up by the outer seven-membered shell of the Cl atom to form one Na^+ ion and one Cl^- ion, each with a stable outer shell of eight electrons. In consequence of their charges, these two ions attract one another and come together as an NaCl molecule.

Landé and Born [22] have developed this idea by taking into consideration the lattice-structure of the NaCl crystal. They succeeded in calculating, from purely physical measurements such as density and compressibility, the heat of formation of one gram-molecule of NaCl from its ions, and from this drew numerous conclusions, many of which are well supported by experiment.*

* The other essays contain more concerning these investigations.

13. The Visible Spectra

Kossel's work has other important applications, particularly in optics. It must be assumed that the visible spectra originate mainly in the outermost electron shells. This granted, it follows that the spectrum of the monovalent ion of an alkali earth, for example (third vertical column in the periodic table), must qualitatively be the same as that of the corresponding neutral alkali atom ; [23] since both have the same inner shell and an outer electron : they differ only by a unit of the nuclear charge. This hypothesis seems to be entirely satisfactory ; thus the spectrum of the He^+ ion must be qualitatively identical with that of the H atom.

14. The Quantum Theory of Atoms

But how are we to imagine spectra to be produced? In the earlier atom-models, such as Thomson's, the electrons had centres of equilibrium, in relation to which they could oscillate; these oscillations were thought to give the frequencies of the spectrum. But Rutherford's atom-model renders such ideas impossible. Above all the stability of such structures is inexplicable, since, according to the laws of the classical theory the electrons encircling the nucleus radiate electromagnetic energy and should therefore always be approaching the nucleus. Thus in no way can the optical spectra be explained by such "self-oscillations" of the Rutherford atoms. Classical mechanics and electrodynamics fail entirely here and must be replaced by something fundamentally new. The correct solution was found by Bohr [24] who ingeniously combined Planck's [25] quantum theory with Rutherford's atom-model.

This is not the place to discuss the development of the quantum theory which likewise originated from the failure of the classical theory to explain certain radiation phenomena, particularly the heat-radiation of glowing bodies. Suffice it to say that Planck was forced to the conclusion that in the

elementary processes of heat-radiation energy is not emitted or absorbed haphazardly, but only in multiples of a quantum $h\nu$; where ν is the frequency of the radiation and h a constant of the value

$$h = 6{\cdot}54 \times 10^{-27} \text{ erg/sec.}$$

This striking hypothesis, which was shown to hold also for processes such as the removal of electrons from metals by the action of light in photochemical processes, was applied without modification by Bohr to the Rutherford atom.

He assumed that there were certain "stationary paths"

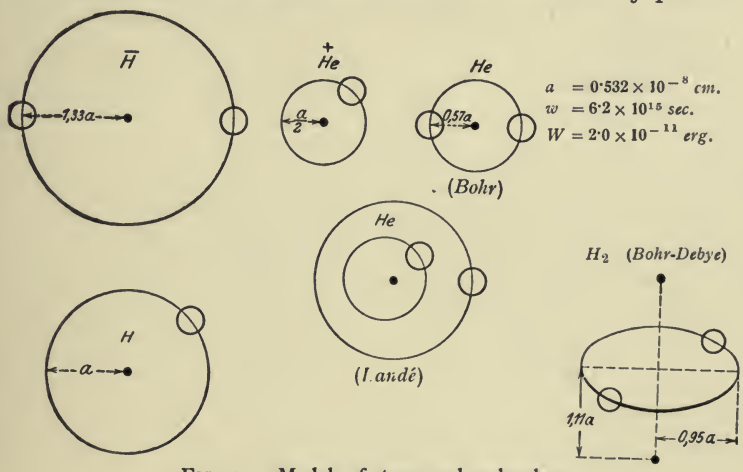


FIG. 21.—Models of atoms and molecules.

in which the electrons could travel round the nucleus without losing energy. Transitions between such stationary paths are intermittent, they produce, as will be shown in detail, the spectrum of the element.

The calculation of these stationary conditions yields exceptional mathematical difficulties, similar to those arising in theoretical astronomy in calculating the paths of the heavenly bodies. An atom resembles a minute solar system in which the sun is replaced by the nucleus and the planets by electrons. Here, however, the sun is not large

compared with the planets; on the contrary, it is exceedingly small, but in both the mass of the system is concentrated in the central body. The atomic attraction is not gravitational but electrical, yet the laws of motion are similar, since Newton's law of gravity is the same as Coulomb's law of electrical forces. From amongst the enormous number of mechanically possible paths the "stationary" ones are defined by certain "quantum rules." For the simplest examples, the H atom and the above-mentioned similarly constructed He^+ ion, Bohr has deduced these rules; for the general case they have been formulated by Schwarzschild,[29] Epstein [30] and others. But the difficulties of calculation have only been completely overcome in the "two body problem" of the H atom and the He^+ ion where Kepler's three simple laws hold. These are:

1. *The electron describes an ellipse, the nucleus being at a focus.*
2. *The square of the period is proportional to the cube of the major axis.*
3. *The surface swept out by the radius vector is proportional to the time.*

To these we must add the quantum laws:

4. *The length of the major semi-axis equals* $\frac{n^2h^2}{4\pi^2me^2}$, *where m is the mass (known) of an electron, e its charge, h Planck's constant, and n an arbitrary whole number* (1, 2, 3 . . .).
5. *The ratio between the area swept out in one revolution to the period equals* $\frac{n^1h}{4\pi m}$, *where m and h have their previous values, whilst* n^1 *is a whole number usually not equal to n.*

For mathematical reasons the number n^1 cannot be greater than n. n is called the chief quantum number and

n^1 the azimuthal quantum number. For $n = n^1$ a circular path is the result; the radius a, the revolution frequency ω and the energy content W of the innermost orbit ($n - n^1 = 1$) can be read from the diagram (Fig. 21). With increasing n there are also elliptical paths which become narrower as n^1 decreases. When an electron jumps from one orbit to another, energy in the form of light is either absorbed or emitted. Concerning the law of this absorption and emission, Bohr has put forward the following hypothesis, which is related to the quantum theory of radiation. At every jump from an orbit of greater energy to one of less, a monochromatic ray is assumed to be emitted, the vibration number of which multiplied by h is equal to the energy W emitted, i.e.:

$$h\nu = W.$$

In this way the emission law of the H atom is quantitatively obtained; Fig. 22 shows this well-known series [26] in two star spectra.[27] The lines of this series are seen between two control spectra; one easily recognises the regular sequence of the lines and their crowding in the ultra-violet, the boundary of the series. The following table shows the

Line.	m.	Calculated.	Observed.	Difference.
$H\alpha$	3	6564·96	6564·97	0·0
$H\beta$	4	4862·93	4862·93	0·0
$H\gamma$	5	4341·90	4342·00	+ 0·1
$H\delta$	6	4103·10	4103·11	0·0
$H\epsilon$	7	3971·40	3971·40	0·0
$H\zeta$	8	3890·30	3890·30	0·0
$H\eta$	9	3836·70	3836·80	+ 0·1
$H\theta$	10	3799·20	3799·20	0·0
$H\iota$	11	3771·90	3771·90	0·0
$H\kappa$	12	3751·40	3751·30	− 0·1
$H\lambda$	13	3735·60	3735·30	− 0·3
$H\mu$	14	3723·20	3722·80	− 0·4
$H\nu$	15	3713·20	3712·90	− 0·3

Comparison of the calculated and observed wave-lengths of the Balmer series.

precision with which the wave-lengths of this series are represented by the formula first found empirically by Balmer, and now theoretically established by Bohr. Innumerable intricacies of the H spectrum, for example, the delicate subseries of the principal lines,[28] dispersion in electrical fields,[29] etc., are explained quantitatively by the development of Bohr's theory by Schwarzschild,[29] Epstein,[30] Sommerfeld[31] and others.

Similarly with the He^+ spectrum; its principal series used to be regarded as a subseries of hydrogen, owing to its analogous structure.

Definite ideas have been evolved concerning the neutral He atom. The spectrum of helium falls into two groups of

FIG. 22.—Hydrogen star spectra (Balmer series).

lines which are so different that formerly they were ascribed to different elements, namely "orthohelium" and "parhelium." It must be a question of two different types of motion of the two electrons around the doubly-charged nucleus. Landé and Bohr have assumed that in the "orthohelium" plane paths and in "parhelium" spatial paths occur.[32] Precise calculation here meets the well-known difficulties of the astronomical problem of the three bodies. It has not yet been possible to deduce a model, the stationary paths of which correctly explain the spectrum of He; even the normal condition, the stationary path of the smallest quantum numbers, of the He atom is not known with any certainty; hence it has not yet been possible to calculate the ionisation-energy of He to agree with the observed value.

This is the work necessary to remove completely an electron from the atom, and is therefore a quantity fundamental to the Kossel conception of chemical combination. It is almost the difference in energy between the extreme quantum orbits, and is, therefore, related to the ultra-violet boundary of the spectrum by the quantum law,

$$J = h\nu$$

where ν is the boundary frequency. Franck and Hertz have shown how to measure directly this separation energy, J,[33] by bombarding the atoms with electrons and observing the speed with which the electrons shatter the atom and thereby lose their energy.

The value for the energy-content, J, thus obtained is then

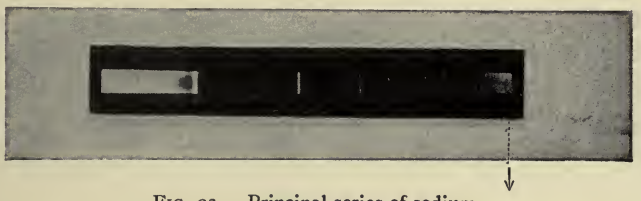


FIG. 23.—Principal series of sodium.

compared with the limit-frequency ν of the series and the relation thus established between optical and electrical measurements and defined by the law $J = h\nu$ is generally satisfactory. Fig. 23 shows the spectrum of the alkali metal Na, in which one can recognise the boundary of the series, the ν of which enters into this law. The exact calculation of the series limit, or ionisation-energy J, from an atom model has, however, been achieved only for the H atom. For the present one has to be content with qualitative observations and rough approximations for atoms of position number 2 and upwards. In this respect Bohr has achieved signal success.[21] In examining qualitatively in the light of partly theoretical and partly empirical considerations, how one electron after the other is taken up in the progress from

element to element, he succeeded in outlining the physical and chemical properties of all the elements in the periodic system. All electrons describe elliptical paths that influence one another; this causes the paths to remain not fixed, but slowly to revolve. The major semi-axis of the path and the revolution frequency of the spectrum are determined by the chief quantum number n, which also determines most of the energy. The eccentricity of the ellipses increases with decreasing azimuthal quantum number n^1, which at the same time determines the revolution or precession of the path. In the centre of each atom from He upwards there is a configuration of two electrons on the 1_1 paths (i.e. those for which $n = 1$ and $n^1 = 1$) similar to that of the He atom. The higher the position in the periodic system the smaller is this inner structure; for with increasing position-number the attraction of the nucleus grows. In Li, the element following He, an electron on a 2_1 path is added (i.e. a more eccentric ellipse with $n = 2$, $n^1 = 1$); in each following element a further electron attaches itself, in a path of the same or another type, according to whether the resulting structure is more stable in the one or the other form. What actually occurs can be read from the spectra almost without ambiguity. In carbon C ($z = 6$) there are four electrons travelling on congruent 2 paths, the planes of these paths are related to one another symmetrically like the surfaces on a regular tetrahedron.

The new electrons then attach themselves in almost circular 2_2 paths, until in neon there are four such paths. Thus the first shell of eight is completed. The next element Na contains a loosely bound electron on a long elliptical 3_1 path. In this way Bohr has deduced highly probable quantum numbers for the electrons present in every element up to the heaviest; even the elements in the iron group with their magnetic properties, and the anomalous rare earths have been explained.

Attempts to construct models of molecules on these lines have not yet yielded any very satisfactory result. Here the mathematical problem consists of the calculation of the electron paths around two or more nuclei, and is considerably more difficult than the corresponding problem with the atom. It has been solved, so far, only for the motion of one electron around two nuclei; this occurs in the H_2^+ ion, which is present in canal rays. The calculation was made by Pauli[34] by disregarding the nuclear motion; however, here experimental results are still too uncertain to be employed to test the theory.

If, instead of a quantitative, only a qualitative prediction of the molecular properties is required, it also can be obtained without much mathematical assistance. The spectra of molecules are of a type quite different from those of atoms; they consist, not of single, isolated lines, but of narrow groups of lines, which are called bands. The laws of these band spectra, have, like those of the line spectra, been explained by the quantum theory; from them the most important properties of the molecules can be deduced, such as the moment of inertia and the frequency of the oscillations of the nuclei in the molecule with respect to one another.

X-ray spectra, from which the first definite knowledge of the regular structure of matter was derived, originate not from molecules but from atoms. The theory of X-ray spectra, which has been developed particularly by Sommerfeld,[35] from measurements by Siegbahn[36] is likewise founded on the quantum theory. Each line of an X-ray spectrum is produced by the transition of the atom from one state to another, in which the energy W thus released is emitted as an X-ray of frequency ν, according to the quantum law, $W = h\nu$. The energy associated with each individual quantum state of the atom can in this way be determined from empirical data. As yet, however, no success has been

achieved in calculating accurately this energy from an atom-model.

15. The Structure of the Nuclei

In conclusion, we will once more touch on the problem of the structure of the nuclei from smaller units. As early as 1815 an English doctor, Prout, formulated the hypothesis that the H atom was the primordial matter from which they are all formed. Later, this hypothesis was allowed to lapse, because the atomic weights were not whole multiples of the atomic weight of hydrogen. However, two reasons are now known for this, one being the existence of isotopes, the other the deduction from the theory of relativity that energy produces mass. Isotopes of the radioactive elements are known ; they are elements of exactly equal nuclear charge-numbers, but slightly different atomic weights. Their chemical behaviour is exactly the same and they form mixtures which appear to be homogeneous elements. Such a mixture, the atomic weights of the constituents of which are whole numbers, would show an atomic weight that was not quite a whole number, but an average value for the constituents. Again, when several nuclei (say He nuclei) come together to form a larger nucleus, energy and therefore mass is displaced. Hence, the total mass of the nucleus is not the exact sum of the parts, but greater or smaller, and consequently not a whole number. This new knowledge now makes it possible to revive Prout's hypothesis, with the modification that the atom-nuclei are assumed to be built up from hydrogen nuclei. Aston [37] has proved experimentally that numerous elements (such as chlorine, neon, mercury, etc.), the atomic weights of which deviate considerably from whole numbers, are indeed mixtures of isotopes, and that the pure isotopes have whole-numbered atomic weights. He achieved this by applying Thomson's canal ray method (mentioned in section 4), which he greatly improved. For

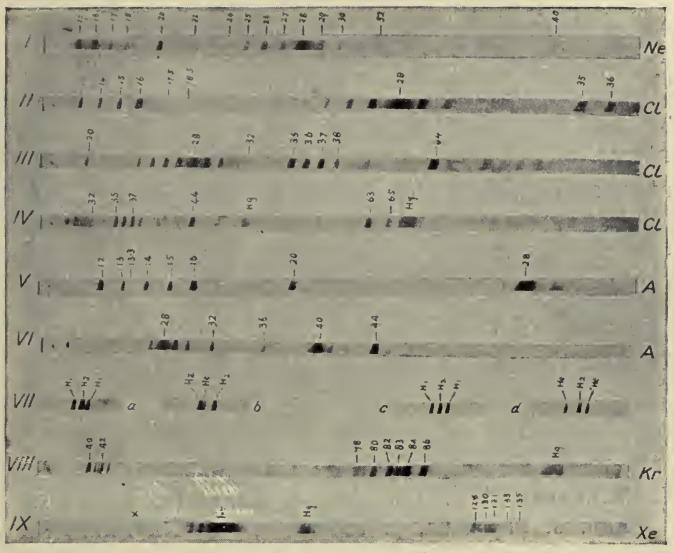


FIG. 24.—Mass spectrograms of neon, chlorine, argon, krypton, xenon. They indicate values of m/e, based on oxygen ($m = 16$).

every atom of definite charge and mass he obtains a particular canal ray, which registers itself on a photographic plate as a narrow band. Fig. 24 shows one of Aston's "mass-spectrograms," which strikingly demonstrate the correctness of the modified Prout hypothesis. Recently Rutherford has succeeded in splitting off H atoms from the N atom.[38] When a gas is bombarded with α-rays, it sometimes happens that an atom is hit centrally, so that it itself attains a high velocity. Particularly is this so when dealing with hydrogen; the H atoms, being four times smaller in mass, travel with greater velocity and farther than do the bombarding α-rays

FIG. 25.—Paths of hydrogen atoms produced by α-rays.

(He nuclei), and there is, therefore, a greater range over which they can be recognised (Fig. 25). When Rutherford bombarded nitrogen gas in this manner, he found such secondary rays of great range, which could be nothing but H atoms. The α-particle must therefore have shattered the N atom and split off an H atom.

This fundamental discovery gives promise that one day it will become clear that all matter is constructed of two polar components. Then all physics and all chemistry will be a branch of the theory of numbers—the theory of the atomic number z.

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FROM MECHANICAL ETHER TO ELECTRICAL MATTER

INTRODUCTION

IT is not long since the literature of physics consisted, for the most part, of papers discussing the mechanical properties of the ether, and the remains of such ideas are with us to this day. On the whole, though, physics has adopted new ideas, which may be summed up in the phrase " matter is electrical."

This involves a fundamental change of thought. What used to be the basic primary (i.e. mechanics), to-day has become the deduced secondary, and, conversely, the ether, which used to seem necessary only for the mechanical explanation of electromagnetic phenomena, has become the sole basis of the science. It is worth while to study this inversion of ideas and determine whether it means an advance in knowledge.

1. The Elastic Theory of Light

The " Physics of the Ether " commenced early in the nineteenth century with the study of " Optics." At that time mechanics had reached that state of perfection which made it the premier science. Apart from the mechanics of the centre of gravity, which reached its zenith in astronomy, the mechanics of the continuously propagated media—the elasticity theory of gases, liquids, and solids—had been evolved. So, not unnaturally, mechanical laws were applied to optical processes. The light waves were compared with

the elastic waves in material bodies; thus arose the first ideas on the elasticity of the ether.

In elastic bodies, however, there are two kinds of waves: those in which the particles oscillate in the direction of the wave-motion (longitudinal waves), and those in which the particles oscillate across the direction of the wave-motion (transverse waves). It can be proved that light waves are transverse; up to the present, no indication has been obtained of optical longitudinal waves. Since longitudinal oscillations are obviously connected with alterations in density, it follows, from the lack of longitudinal light waves, that the ether cannot, like a gas, be compressed; on the other hand, it must be exceptionally elastic, as it propagates transverse waves as readily as a solid body.

It was therefore concluded that "the ether is an incompressible, perfectly elastic, solid body." Yet, in spite of this, the heavenly bodies move through it at an enormous speed, wholly without friction and disturbance.

Apart from this anomaly, other difficulties arose in the application of the elastic light theory so that it was readily superseded by the electromagnetic theory put forward by Maxwell.

2. The Electromagnetic Theory of Light

In this theory the ether is no longer regarded as an elastic body, but it is still assumed to be a continuously propagated medium with definite properties, which appear in phenomena as electromagnetic fields. Rapid oscillations of the fields are light waves; their speed can be ascertained by purely electromagnetic measurements.

This theory necessitates considerable mental abstraction. What really is this ether which, although a continuous medium, is different from all known bodies, gaseous, liquid, or solid? Application of a theory necessitates imaginable representation; Maxwell met this difficulty by using

mechanical models to explain certain properties of the ether. Later, the problem of reducing Maxwell's ether to a mechanical basis became a science of its own. Bjerknes was especially successful; he regarded the ether as a fluid containing electrical charges as pulsating spheres, a view that was extended by Korn and still exists.

But no fresh discoveries were made in this direction; however, interest might yet have been maintained had not the theory of relativity made the idea of a material ether absolutely impossible. This theory necessitates a still deeper abstraction, a greater departure from the usual conceivability, and therefore many a physicist looks back with regret to the halcyon days of the solid ether.

3. The Theory of Atoms

Knowledge can advance through abstractions, but in the main it does so by actual perception, and if this theory had done nothing more than prove the impracticability of mechanically representing the ether and its properties, it would not have done much. But a survey of physics during the past few years shows plainly that the art of experimenting has achieved its greatest successes when in closest touch with this theory, so it must stimulate the imagination more than did the old mechanical representation of the ether. The " electromagnetic universe " of present-day physics may be called abstract in its foundations; in its superstructure it is rich in concrete forms, due to the union of Maxwell's abstract representation of the ether and of the theory of relativity with the theory of atoms.

To-day not only is matter regarded atomically, but even electricity itself has been resolved into atoms, called electrons. Now, the idea of atoms and electrons is easy to grasp; even those who distrust the mass of formulæ involved in Maxwell's theory of electricity can operate successfully with the movements and interactions of electrons and atoms. The most

recent development of these ideas is the attempt to construct the atoms themselves from electrons; in this Planck's quantum theory plays an important part.* We will go no further into these investigations, but we will mention some advances which throw light on the transition from the mechanical to the electrical conception of physics.

4. The Lattice-theory of Crystals

These advances deal with the constitution of solid bodies and the nature of the forces holding them together. Solid bodies are either amorphous (vitreous) or crystalline. However, we now regard only crystals, or conglomerations of crystals, such as most of the metals, as solids in the real sense of the word; amorphous substances have come to be looked on, in many respects, as particularly viscous liquids.

The criterion of a crystal lies in its regular structure from atoms and molecules. This structure can, as Laue discovered,† be rendered visible on a photographic plate by means of X-rays. Fig. 1 shows such a photograph of a rock-salt crystal (NaCl). We now know the ultimate structure, or lattice, of a large number of crystals; rock-salt, for example, is built up, as shown in Fig. 2, from sodium and chlorine atoms, like a chess-board in three dimensions. Crystals, therefore, are not continuous media. It is a problem the solution of which has not been easy to obtain, that such space-lattices behave mechanically like the continuous solids of the old elasticity theory. The foundation of the

* A detailed account of the quantum theory and its application to the structure of atoms can be found in "Naturw.," 6, part 17 (1918). See also the previous essay.

† References to this discovery and its development have appeared in "Die Naturwissenschaften"—H. Löwy, 1st year, p. 105 (1913). A. Sommerfeld, 4th year, pp. 1, 13 (1916). F. Rinne, 5th year, p. 48 (1917). M. Siegbahn, 5th year, pp. 516, 528 (1917), and also numerous other papers.

mechanical ether theories has thus been destroyed, for these latter originated using continuous solid bodies as an

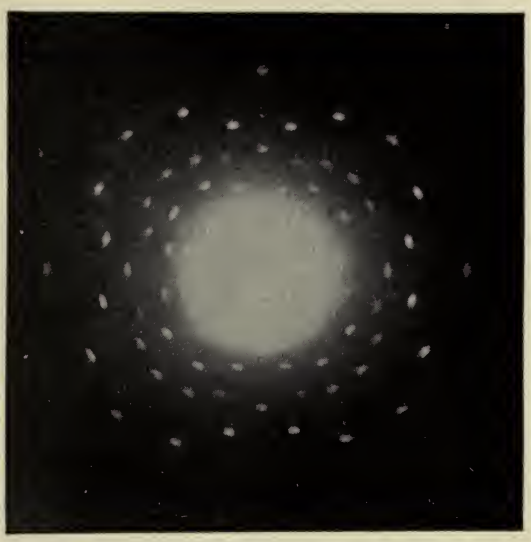

FIG. 1.—Laue photograph of rock-salt (NaCl).

experimental basis so that all ether phenomena could be referred to the properties of such media. But the continuous elastic substances are simply delusions produced by the crudeness of our senses; they are, in reality, discrete lattices, with spaces between their atoms. If these spaces are imagined to be filled with ether, there is no sense in ascribing to the latter properties corresponding to those of the lattices themselves regarded as continuous substances, for this is only arguing in a circle.

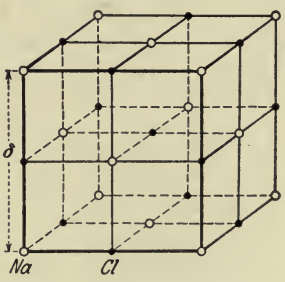

FIG. 2.—Lattice of rock-salt.

Therefore, present-day physics takes a different view, which not only is more consistent, but also has led to tangible results. The electromagnetic field in the ether is taken

empirically, and the solid body the crystal, regarded as a regular arrangement of electrical charges which react on one another according to the field-laws. From this originate those crude properties which the crystal-lattice has in common with the continuous elastic substances of the old mechanics.

5. The Electrical Nature of Molecular Forces

This leads to the conclusion: "*The mechanical, elastic forces of solid bodies are actually electrical.*" If we know the charges of, and the intervals between, the atoms in the crystal-lattices, all the electrical interactions are fundamentally determined; it must, therefore, be possible quantitatively to predict the elastic properties.

Here we pass from theoretical considerations to problems, the solutions of which, although not readily obtained, have proved the superiority in many respects of the new standpoint.* The connections between all manner of mechanical, thermal, electrical, and optical properties of the crystals had to be explained on the basis of the lattice theory, and mathematically reduced to the forces between the individual constituents of the crystal-lattice.[1] The most important results of these investigations will be described for the above-mentioned rock-salt crystal.

6. Atom Lattices

As we have already seen, the lattice of this crystal is not composed of NaCl molecules, but of individual Na and

* Similarly in the kinetic theory of gases there was the contrast between the theories of continuous substances and of atoms; both were equally useful so long as the latter could represent only the formal connections. The atomic conception prevailed when it succeeded in determining numerically the coefficients of formulæ such as the ratio of specific heats, the relation of the coefficients of thermal-conductivity and internal friction, etc.

Cl atoms (Fig. 2). This is proved, not only by Laue's X-ray photographs, but also by the thermal behaviour of the crystal. The energy of a body consists in the motions of its smallest constituents; in crystals, these vibrate about their centres of gravity. According to a fundamental law of statics, the energy of these vibrations is divided amongst the individual constituents so that in time each and every constituent possesses *the same* amount of energy which can be determined from the kinetic theory of gases. From thermal measurements one can deduce the number of particles, each containing this amount of energy, which must be present in unit mass, so that this may contain the observed heat-content. In this way it was proved that the constituents cannot be NaCl molecules, for the unit mass would then contain only half as many particles, and consequently only half the observed heat-content, as it would if they were atoms.

7. Electrolytic Ions

If rock-salt is dissolved in water the solution becomes a conductor of electricity—an electrolyte. Such a conductor differs from a metallic one in that the passage of a current is connected with the transport of the dissolved substance. This is shown by the fact that sodium is liberated at one electrode and chlorine at the other. Faraday discovered the law governing this process; he found that the passage of a definite amount of electricity was always accompanied by the appearance of the same amount of the two substances in quantities chemically equivalent and necessary for the combination, NaCl. This process is regarded as being atomic, it being assumed that every atom transports the same amount of electricity; the Na atom carries a positive, and the Cl atom a negative, atom of electricity. Such charged atoms are called "ions." The atom of electricity is to be observed in many other phenomena, but, in every

instance, it is the negative one ; this is called the " electron." The positive charge is always bound to matter ; the neutral atom consists of one positive nucleus surrounded by a number of electrons. The Cl^- ion is, so to speak, the chemical combination of a neutral Cl atom and one electron. The positive Na^+ ion must be imagined to be formed by removing one electron from the neutral Na atom. The magnitude of the charge of the individual electron is a universal constant e, which can be determined in several ways, and is equal to $4{\cdot}77 \times 10^{-10}$ E.S.U.

8. Ion Lattices

If such a NaCl solution is evaporated so that the rock-salt crystallises out the process consists of the individual Na and Cl atoms uniting to form the above-mentioned lattice. What happens then to the charge of the atoms ; do these cancel one another, or do the atoms retain their ionic character in the solid state as well ?

Madelung [2] has answered this question by the interpretation of an optical property of crystals such as NaCl. Imagine a piece of rock-salt placed between two parallel, charged, metal plates ; then the lattice shown in Fig. 2 is exposed to an electrical field (Fig. 3). If we assume that the Na atoms are positively, and the Cl atoms negatively, charged then the former will be attracted in the direction of the field, and the latter in the opposite direction. Owing to the rigidity of the crystal, this attraction will produce only a very small relative displacement of the Na and Cl ions. Now consider the well-known phenomenon of resonance : if a pendulum is allowed to oscillate freely in its natural period, the amplitude can be

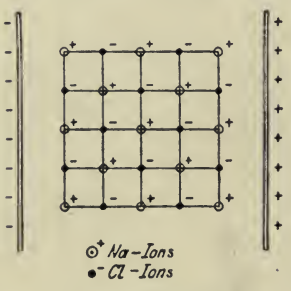

Fig. 3.—Rock-salt lattice in an electrical field.

increased with a minimum of work. In the same way, an oscillating electrical field of suitable period will cause a maximum displacement in the crystal. Light-waves are such oscillating electrical fields; it is to be expected, therefore, that light of a suitable wave-length will appreciably affect the crystal, and *vice versa* be affected by it. Rubens has proved this[3]; he found that infra-red light of a very long and definite wave-length is strongly reflected by the crystal, whilst light having a slightly different frequency is unaffected. By repeated reflections he was able to isolate this selective light, and on this account called it the "residual rays."

These residual rays proved that the atoms of the crystal were charged. That this charge for crystals of the type NaCl is exactly one electron, has been shown by calculating the known frequency of the light from the charge of the electron, the masses of the ions and the measureable elastic forces of the crystal.[4]

Recently, however, the ion-charge has been tested directly by Debye and Scherrer, by means of X-ray photographs.[5] The X-rays perturb the electrons of the atom, thus producing secondary rays, which proceed from the atom; these, by reason of their interference, produce the phenomena discovered by Laue (Fig. 1). The intensity of the interference spots will depend on the number of electrons present in the atoms; conversely, by measuring the intensity of the interference spots, conclusions can be drawn as to the number of electrons the atom contains. In this way it has been shown that, in the crystal of lithium fluoride, the Li atom has one electron less, and the F atom one more, than in the neutral state. Similar conditions undoubtedly exist in all compounds of the alkali metals (Li, Na, K, Rb, Cs) with the halogens (F, Cl, Br, I).

9. The Electrical Force of Contraction

We have now collected those facts regarding the constitution of crystals necessary for an absolute calculation of their mechanical properties from electrical data.[6]

If the rock-salt crystal (Fig. 2), with its oppositely charged Na and Cl atoms, be examined, it will be obvious that there necessarily follows from these charges an effort by the lattice to contract, for the adjacent, oppositely charged particles attract one another. Admittedly, particles having the same charge repel one another, but appreciably less strongly, because they are further apart, and electrical force, according to Coulomb's law, varies inversely as the square of the distance.

The calculation of this contractile force has recently been achieved by Madelung in the following way.[7] First, imagine all the ions to be at an infinite distance from one another, and then infinitely slowly to come together to form the crystal lattice. Because of the contractile force they yield a certain amount of energy, depending on the absolute dimensions of the lattice. If δ be the distance between two similar ions on the same edge of a lattice-cube of a crystal of the type NaCl, the value found for this work is $1{\cdot}7{\cdot}94\ e^2/\delta$, where e, as above, is the charge of the electron.

10. The Force of Repulsion

Now, the ions remain at this distance, δ, and do not completely come together. This can be explained only by a force of repulsion, which increases as the distance diminishes and finally attains equilibrium with the contractile force. Considerations of a general nature lead to an expression of the form b/δ^n, where n is a whole number and b a constant, for the work necessary to overcome this force of repulsion in the above process of building up a crystal from its isolated ions. The exact law of the force can be deduced when it

depends on the mutual action of the electrical charges in the atom, and it can be represented with great approximation by such an expression.

The constant b depends on the distance between the ions. To make this clear, take a bow (Fig. 4) to illustrate the equilibrium of a contractile and an expanding force. The wood endeavours to straighten, and the string tends to draw the ends together. Given the flexure-force of the wood and the elasticity of the string, we can calculate from them the shape of the bow and the length of the string, which is analogous to the distance δ between the ions, when in equilibrium. If we know the length of the string and Young's modulus for it, but do not know the elasticity-

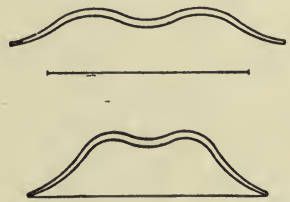

FIG. 4.—Equilibrium between string and bow.
Released bow / Bent bow.
Unstretched string / Stretched string.

modulus of the bow, then, conversely, we can calculate the flexure-force of the bow. This exactly corresponds to the conditions in a crystal; the force of contraction is known, the distance δ between the ions can readily be calculated from the density and the atomic weight. It follows, therefore, that the conditions for equilibrium yield the data for the calculation of the repulsion force b/δ^n. The only unknown remaining is the exponent n.

11. The Calculation of the Compressibility

So, except for n, the energy given out by the ions in the formation of the crystal is known, and hence all the properties of the crystal depending on the distance δ between the

ions can also be determined from the general laws of dynamics. If the crystal is subjected to the same pressure on all sides it becomes compressed ; this change in volume * obviously depends only on the variation of the distance δ between the ions, and it should be possible to deduce it from the above principles. The ratio of the decrease in volume to the corresponding increase in pressure is called the compressibility, and is indicated by x. It is, therefore, possible, by choosing a suitable integral exponent n, to calculate this x from the charge e of the electron and the distance δ between the ions, which, as stated above, is determined from the density and atomic weight. With $n = 9$ a very good agreement has been obtained, as is shown in Fig. 5.[8] Here the compressibilities obtained by Richards and Jones,[9] in units of 10^{-12} dyns./cm.^{2}, are indicated by crosses ; dashes mark the values calculated from the above theory.

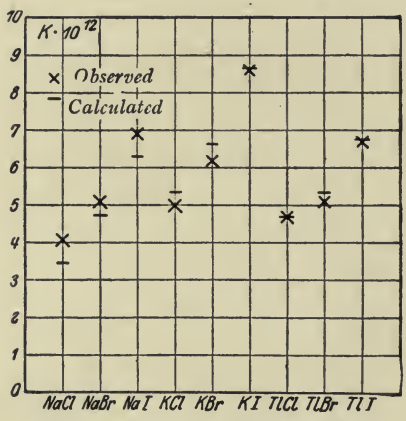

FIG. 5.—Compressibilities of the alkali halides.

This proves that the elastic resistance to compression depends on electrical forces and can be calculated. This result may be generalised.

A great deal could still be said on the significance of the exponent $n = 9$. It throws much light on the inner structure of the ions, which most probably are not systems of electronic

* In our example of the bow, this alteration in volume corresponds to the approach of the ends of the string when the bow is bent for shooting. With a given bending force this is obviously determined by the elastic properties of bow and string.

rings in the same plane as in Bohr's earlier models, but have rather the form of cubes. The number 8 of the cube-corners is probably closely connected with the periodic system of the elements, in which each of the first two periods contains 8 elements.[10] Relations have been shown to exist between heats of chemical reaction and ionisation-tensions,* and also among other properties. However, a discussion of these ideas would extend beyond the limits of this essay, but enough has been said to show that science has turned with advantage from " mechanical ether " to " electrical matter."

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* The ionisation-tension is that tension which is necessary to free an electron from an atom (Franck and Hertz, " Verh. d. Deutsch. Phys. Ges.," **15**, 34, 1913); it is a characteristic constant of the atoms. Cf. the other two essays in this book.

THE FUSION OF CHEMISTRY AND PHYSICS

1. The Problems of Chemical Affinity

THE most important task of physical chemistry is the determination of the magnitude of the forces of chemical attraction—affinities—and thence the prediction of the course of reactions. The development of this field of investigation resolves itself into distinct stages which run parallel with the advances of thermodynamics.* [1]

The first stage is marked by the application to chemical processes of (1) *the first law of the theory of heat—the law of the conservation of energy.* Berthelot and Thomsen believed they had discovered a measure of the affinity in the heat-change in a reaction. Berthelot (1867) formulated the principle : " Every chemical change results in the production of such substances in the formation of which most heat is evolved." But this hypothesis could not be maintained ; in particular, it could not explain the large class of endothermic reactions in which no heat is evolved, but which proceed with the absorption of heat.

The next stage in the study of chemical affinity corresponds to the development of (2) *the second law of the theory of heat—the law of entropy.* Van't Hoff (1883) recognised that the real measure of affinity was the work yielded under the most favourable conditions, i.e. when a chemical reaction is carried out reversibly at constant temperatures. Helmholtz called this work " free energy " ; its temperature coefficient

* J. Eggert has given a good review of the evolution of thermochemistry up to and including Nernst's theory in " Die Naturw.," 7, 883 (1919).

is called entropy. Van't Hoff's definition has been fully substantiated, and has made possible, from a small number of measurements, the prediction of the course of chemical reactions under varying temperature, pressure, and other external conditions. These measurements are, with one exception, of a purely physical nature, being determinations of heats of reaction and specific heats. The one exception is chemical affinity which has to be measured at one temperature before it can be calculated for all other temperatures from the laws of the thermo-dynamics.

Nernst was the first to solve the problem of eliminating this chemical measurement, thus reducing the calculation of affinities to purely physical dimensions, and so he initiated *the third stage* in the development of thermo-chemistry. The practical importance of Nernst's theory, and its relation to the latest development of the science (the quantum theory), justify its being designated as *the third law of the theory of heat.** Nernst's hypothesis is that this necessary determination of affinity at *one* temperature can be replaced by a general law for the behaviour at very low temperatures. From general thermo-dynamic principles the curves which represent the variation of heat of reaction and affinity with temperature meet at absolute zero; according to Nernst they are also tangential at this point. This means that at very low temperatures Berthelot's hypothesis is true; from this the affinity curve can then be determined for all temperatures.

This, indeed, is a great achievement—the determination of chemical processes by purely physical measurements. It is a fusion of chemistry with physics, which apparently leaves nothing to be desired.

But there yet remains another problem, the solution of which must always be an ideal of the physicist—the proof of

* More concerning this can be found in Eggert's essays.

the unity of all physical and chemical forces and their reduction to reactions between the elementary components of matter—electrons and atoms, or atom-nuclei.* Modern physics already possesses models of the atom, which certainly approximate to the facts, and with these it can explain numerous mechanical, electrical, magnetic, and optical phenomena. It must not stop with these, but must endeavour also to reduce chemical properties to atomic forces, in so far as they are known. In this respect Nernst's theory is a good starting-point, for it reduces the complexity of chemical processes to a series of simple constants. It is now the task of the molecular physicist to calculate from the properties of the atom these constants which the physical-chemist can determine by calorimetric and similar measurements. This opens up an extensive field of thermo-chemical investigation.

2. The Elementary Chemical Constants

In order to survey what already has been done in this field, and what is still outstanding, we will consider, as an example, a reaction in which two monatomic gases A and B unite to form the gas AB:

$$A + B = AB.$$

The converse process is the dissociation of the substance into its components.

Both processes lead to an equilibrium, in which all three substances are present with definite partial pressures, p_A, p_B, and p_{AB}. To this equilibrium the law of mass-action applies, i.e. the ratio

$$\frac{p_A \times p_B}{p_{AB}} = K_p \qquad . \qquad . \qquad . \qquad (1)$$

for a given total pressure p has a definite value which depends only on the absolute temperature. This relation can be

* Cf. the first essay in this book: "The Atom."

ascertained from the three laws of thermo-dynamics, and it is found that

$$\log K_p = -\frac{Q_o}{RT} + \frac{c}{R}\log T + C \quad . \quad . \quad (2)$$

where R is the absolute gas-constant (about 2 cals.), and Q_o, c, and C are three constants, which have the following meanings :—

1. Q_o is the heat of reaction at absolute zero, i.e. the amount of heat evolved at very low temperatures by the combination of 1 mol of A with 1 mol of B to form 1 mol of AB. Q_o can, therefore, only be found by extrapolation from the heats of reaction measured at higher temperatures.

2. c is obtained from the molecular heats at constant pressure of the three reacting gases c_A, c_B and c_{AB} as follows :

$$c = c_A + c_B - c_{AB}.$$

3. C is similarly related to what Nernst calls the chemical constants of the gases, C_A, C_B, and, C_{AB} :—

$$C = C_A + C_B - C_{AB}.$$

The chemical constant of a gas depends on the saturation pressure p of the gas in equilibrium with its liquid. This pressure p decreases very rapidly with the temperature ; and, indeed, at low temperatures the following formula, analogous to (2), holds :

$$\log p = -\frac{\lambda_o}{RT} + \frac{\gamma}{R}\log T + C$$

where λ_o is the limit value of the latent heat of the vapour with decreasing temperature, and γ is its temperature coefficient, i.e. $\lambda = \lambda_o + \gamma T$. The constant C occurring here is the chemical constant of the gas ; it can be determined empirically for every gas by measurement of its saturation pressure.

Hence the three constants Q_o, c, and C are composed of directly measurable quantities, so that the constant, K_p, of

the law of mass-action is reduced to purely physical measurements.

Now commences the task of the theory of atoms, namely, to predict the three constants Q_o, c, and C, or, alternatively, their components, from the properties of the atoms A and B. This problem has been solved for c and C. For some time the specific heats of the gases have been reduced, by the kinetic theory of gases, to the simplest properties of the molecules, namely, to the number of "motion-freedoms" or degrees of freedom they possess. A monatomic gas, for example, has three degrees of freedom—potential displacement in three directions at right angles to one another; for it the kinetic theory of gases yields for the specific heat at constant pressure the value $\frac{5R}{2}$. It can be assumed that the problem of the atomic calculation of specific heats is fully solved, not only for gases but also for solids.

Again, there is no reason why the chemical constant C should not be calculated theoretically. The first deductions were made by Sachur [2] and Tetrode,[3] using the quantum theory, but some doubt was attached to their results. Then, however, Stern,[4] using a method free from objection, showed that the same formula for C can be obtained by a combination of thermo-dynamics and the kinetic theory of matter.

Although C is defined by the formula given above for the saturation pressure, it does not depend on the condensed liquid, but only on the gas, and, for a monatomic gas,

$$C = \log \frac{(2\pi)^{\frac{3}{2}} \times R^{\frac{5}{2}}}{N^4 h^3} + \frac{3}{2} \log \mu$$

where μ, the atomic weight, is the only term depending on the gas; otherwise only universal constants occur, viz. the gas constant R, the number N of the molecules in the mol (Avogadro's number), and Planck's constant h.

Similar formulæ hold for polyatomic gases. In these

the moment of inertia of the molecule and also the relative oscillation numbers of the atoms in the molecule are included.

There remains only Q_o to be discussed. This is, indeed, a fundamental problem in the theory of the atom; its general solution is still far distant. In recent years, however, several very promising attempts have been made which will perhaps form the starting-point of *the fourth and last stage of the theory of heat.* A short account of them will now be given.

3. The Combination-energy of Diatomic Molecules

The heat of reaction at absolute zero Q_o can also be defined as the difference between the sum of the potential energies * of the separated atoms A and B and that of the molecule AB, or, alternatively, as the work that must be applied to decompose the molecule into the atoms A and B (all quantities being multiplied, of course, by the number N of the atoms in the mol). In order to calculate Q_o, the forces ot attraction which the atoms A and B exercise towards one another must, of course, be known. Unfortunately, our knowledge of these forces is very limited; only for substances, the molecules of which can easily be split up into ions, have we any knowledge of the nature of atomic forces. These compounds are, as suggested by Abegg,[5] called *heteropolar;* examples are salts of the type NaCl, which dissociate into the ions Na^+ and Cl^-, or the allied acids such as HCl, in which H^+ replaces the metal ion. Compounds that do not possess this electropolar character are called *homopolar;* examples of these are the elementary gases H_2, N_2, O_2, Cl_2, etc., and compounds, the components of which are similar, such as IBr. The nature of the forces holding the homopolar

* Values for heat, energy, and work are referred to dimensions of the same kind, and are calculated in kg.-cals The mechanical dimensions are converted by dividing by the mechanical equivalent of heat.

compounds together can only be surmised; but it is probable that between the components of a heteropolar compound they are electrical. Kossel*[6] has systematically investigated this, and has proved that, by this hypothesis, a large portion of inorganic chemistry is explained physically.

Thus the fundamental hypothesis is that the heteropolar molecules are actually "ion-compounds," i.e. they are formed by two consecutive processes. First, the neutral atoms exchange one or more electrons, thereby becoming ions, and then these ions owing to their unlike charges, attract one another, according to Coulomb's law of electrostatics, and become attached. Only this second process is referable to known physical forces; the first is entirely theoretical, and can be pictured only in those few instances where a well-established atom-model is available, e.g. the neutral H atom and the He^+ ion.† We will now assume that we are given 1 mol of positive ions, say H^+, and 1 mol of negative ions, say Cl^-, both being in infinite dilution (as "ion-gases"), and it is desired to calculate, on the basis of Kossel's hypothesis, the heat evolved in the combination of these to form 1 mol of HCl gas. In order to illustrate the law of attraction, let us imagine the Cl^- ion to be fixed, and make a diagram (Fig. 1) in which the distance r between the H^+ ion and the Cl^- ion is the abscissa and the potential energy ϕ of the mutual electrical attraction is the ordinate. According to Coulomb's law, if e is the ionic charge, ϕ is represented by the equilateral hyperbola

$$\phi = -\frac{e^2}{r} \quad . \quad . \quad . \quad . \quad (3)$$

which lies entirely below the abscissa. It will make the

* Kossel has recently given an account of his theory in an essay, "On the Physical Nature of the Valency-forces," "Die Naturw.," 7, p. 339 (1919).

† Cf. Section 6 below.

action of this potential energy clear to imagine the H^+ ion to be an infinitely small sphere which rolls on the ϕ hyperbola as on a slide; then, obviously, the sphere will roll towards the Cl^- ion until it is stopped by it. If the latter be a sphere of radius r_o, then in the figure the Cl^- ion is represented by a parallel to the axis $r = 0$, at a distance r_o; beyond this the rolling H^+ ion may not pass. It will, therefore, remain at the point where this line intersects the hyperbola, and the ordinate of this point ϕ_o is the energy (heat)

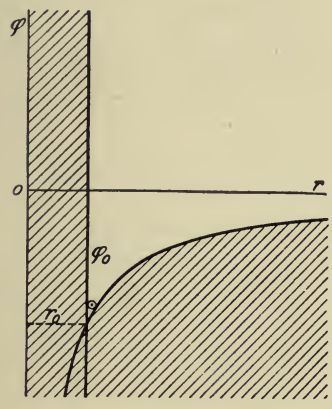


FIG. 1.—Illustrating the law of attraction, $\phi = -\frac{e^2}{r}$; $r > r_o$.

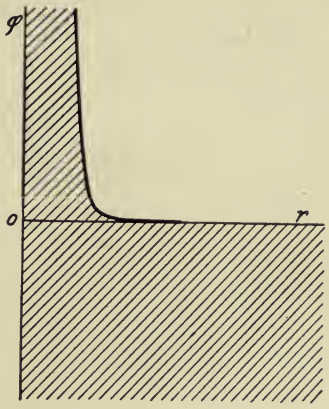


FIG. 2.—Illustrating the law of repulsion, $\phi = \frac{\beta}{r_n}$.

radiated by the combination of the two ions. We have, therefore,

$$\phi_o = -\frac{e^2}{r_o} \quad . \quad . \quad . \quad . \quad (4)$$

Now this picture of the atomic forces is too crude, for one cannot assume that the ions behave like infinitely hard spheres, otherwise liquids and solids (NaCl, etc.) formed from them would be incompressible. So in place of a hard shell it is more reasonable to postulate a repulsive force

which, at great distances, is indefinitely small and does not increase infinitely rapidly. The analogy of the Coulomb forces gives for the potential energy :

$$\phi = + \frac{\beta}{r^n} \quad . \quad . \quad . \quad . \quad (5)$$

where β and n are constants. This is a hyperbolic curve (Fig. 2) lying above the abscissa, the negative slope of which increases with the exponent n. If we again regard this curve as a slide, the H^+ sphere placed on it will roll to infinity, thus illustrating the nature of the repulsive force.

Actually, there are both attraction and repulsion, and the potential energy is given by the equation

$$\phi = - \frac{e^2}{r} + \frac{\beta}{r^n} \quad . \quad . \quad . \quad (6)$$

the graph of which is obtained by the algebraic addition of the ordinates of the two component (dotted) curves (Fig. 3). This gives a curve which has a minimum value where the H^+ sphere, laid upon it, will remain in equilibrium with the abscissa r_o and the ordinate ϕ_o. Using the differential calculus we obtain between r_o and ϕ_o the relation

$$\phi_o = - \frac{e^2}{r_o}\left(1 - \frac{1}{n}\right) \quad . \quad . \quad . \quad (7)$$

The first approximate formula (4) must, therefore, be completed by the factor $\left(1 - \frac{1}{n}\right)$.

In order to apply this formula (7) to the energy of combination, the following conditions must be fulfilled. The interacting ions must be regarded as point-charges and (2) r_o as well as n must be known. In gas molecules such as HCl the H^+ ion is a simple single-charged nucleus: it can be regarded as a point; the Cl^- ion, however, consists of a

nucleus surrounded by 18 electrons, and is therefore an extensive structure, the form of which will presumably be markedly influenced by its neighbour the H^+ ion, so that the charge of the electrons cannot be assumed to be concentrated in the centre. If in spite of this it were desired to apply equation (6), it would still be impossible, for although the nuclear distance is known accurately from the theory of the infra-red band spectrum emitted by the molecule, the exponent n is not.

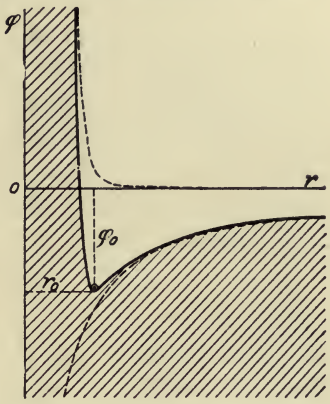


FIG. 3.—Illustrating simultaneous attraction and repulsion,

$$\phi = -\frac{e^2}{r} + \frac{\beta}{n}.$$

Hence the theory cannot yet be used in this form. An advance on Kossel's hypothesis in a quantitative direction was only possible when the theory of the ionic structure of crystals was utilised.[7]

4. The Energy of the Crystal-lattice

Instead of the halogen acid HCl, we will consider the allied alkali salt NaCl, which forms regular crystals having a well-known lattice-structure. We know that the lattice is built up from the ions Na^+ and Cl^- like a chessboard in three dimensions (Fig. 4),* and we have several reasons for assuming that the forces of cohesion holding the lattice together are similar to the chemical forces binding the

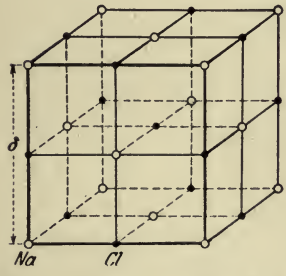


FIG. 4.—The crystal-lattice of sodium chloride; o = sodium ions, ● = chlorine ions.

* Cf. the previous essay, p. 41.

molecule NaCl in the vapour of the salt. In the crystal each ion is symmetrically situaetd with respect to its neighbours; if, by reason of the electrostatic forces, it is displaced, only similar and equal expansion or contraction can occur, so that the general symmetry remains unaltered. Hence the ions can be replaced by point-charges. Between any two ions then there will be an energy-potential of the same kind as that already indicated for the two ions of the HCl molecule (6), i.e. an expression of the form

$$\phi = \pm \frac{e^2}{r} + \frac{\beta}{r^n}.$$

We must remember that like ions (e.g. Na^+, Na^+, or Cl^-, Cl^-) repel one another, so, in the first term, we take for them the positive sign, whereas for unlike ions (e.g. Na^+, Cl^-) the negative sign (attraction) is again used. As adjacent ions are always of unlike charge, the first term will give for adjacent ions a force of contraction, the second term then represents the opposing force which prevents the collision of the ions.

Now comes the mathematical problem of calculating the potential energy of the whole lattice from the mutual interaction of any two ions. It is obvious that the solution must be of the form

$$\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n} \quad . \quad . \quad . \quad (8)$$

where δ is the lattice constant, i.e. the distance from one ion to the next like ion on the edge of the cube (Fig. 4), and a and b are constants obtained by the summation of e^2 and β. Madelung has given a simple method for calculating the constant a of the electrostatic term [8]; it is, of course, proportional to e^2 and depends only on the structure of the lattice. For a lattice of the type NaCl, if Φ is the potential energy for each elementary cube of edge δ, it comes to

$$a = 13{\cdot}94e^2 \quad . \quad . \quad . \quad (9)$$

It will be seen that Φ depends on δ in exactly the same way as ϕ depended on r (6). Hence all the above deductions can be transferred, *mutatis mutandis*, to the lattice. To particularise, the following connection between the equilibrium value δ_0 of the lattice-constant and the corresponding energy for each elementary cube can be established, cf. (7) :

$$\Phi_0 = -\frac{a}{\delta_0}\left(1 - \frac{1}{n}\right) \quad . \quad . \quad . \quad (10)$$

We are now in a position to utilise this formula. The lattice-constant δ_0, for the crystal in its natural undeformed condition, is accurately known, for if μ_+ and μ_- be the atomic weights of the two component ions, then $\frac{\mu_+ + \mu_-}{N}$ is the mass of one molecule of NaCl, and, since the elementary cube contains four (Fig. 4), the mass contained in this cube is

$$\frac{4(\mu_+ + \mu_-)}{N} = \rho\delta_0^3 \quad . \quad . \quad . \quad (11)$$

where ρ is the density of the crystal ; from this δ_0 can be calculated.

The exponent n can also be accurately determined, for it is obviously connected with the slope of the repulsion curve (Fig. 2). Referring yet again to our example of a sphere on a slide, if we displace the sphere from the point of equilibrium (Fig. 3) towards the other ion, we must push it up the steep slope shown in the figure; this obviously depends on n. With a crystal this process is accompanied by a diminution of the lattice-constants, and is therefore a compression. Hence the exponent n is closely connected with the compressibility κ of the crystal. Actually, calculation yields the equation

$$\kappa = \frac{9\delta_0^4}{a(n-1)} \quad . \quad . \quad . \quad (12)$$

from which n can be determined if κ is obtained experimentally.

It has been found * that for all alkali-halogen salts of the type NaCl we may, with sufficient accuracy, take

$$n = 9.$$

Thus all data necessary for the calculation of the energy U, evolved as heat by 1 mol in its formation from ions, are known.[9] U is obtained from Φ_o by multiplication by $-\frac{N}{4}$, because the elementary cube contains four ion-pairs (molecules):

$$U = \frac{Na}{4\delta_o}\left(1 - \frac{1}{n}\right) \quad . \quad . \quad . \quad (13)$$

If we now insert the values for a and δ_o from (9) and (11), and also the known Avagadro number N and the electrical elementary quantum e, we obtain

$$U = 545 \sqrt[3]{\frac{\rho}{\mu_+ + \mu_-}} \text{ kg.-cals.} \quad . \quad . \quad (14)$$

By inserting, for different salts, the atomic weights of the component elements and the densities of the crystals, their heats of formation from ions can be calculated. The values (in kg.-cals.) for the salts NaI and KI are found to be

$$U_{NaI} = 158\,; \; U_{KI} = 144.$$

These refer to absolute zero, as the ions are assumed to be at rest in the calculation of their equilibria. Unfortunately, U itself cannot be measured directly; there are, however, several ways of relating it to observed heats of reaction and other energy constants.

* Cf. the previous essay, p. 48.

5. Reactions between Binary Salts

We will now deal with a chemical process that can be regarded as consisting exclusively in an interchange of ions. The heat of reaction of such a process must be composed of the algebraic sum of the corresponding values of U.[9] Let us consider, for example, the reaction

$$NaCl + KI = NaI + KCl \quad . \quad . \quad (15)$$

This can be supposed to proceed as follows: First, each mol of the solid crystals NaCl and KI splits up into the free ions Na^+, K^+, Cl^-, and I^-, for which work $U_{NaCl} + U_{KI}$ must be supplied. From the free ions Na^+, K^+, Cl^-, and I^-, 1 mol of each of the crystals NaI and KCl is built up, whereby energy $U_{NaI} + U_{KCl}$ is liberated. The total heat evolved—the measureable heat of reaction—is therefore

$$Q = U_{NaI} + U_{KCl} - U_{NaCl} - U_{KI} \quad . \quad . \quad (16)$$

The proof of the theory in this manner is only possible when the values of both U and Q are accurately known, because $U_{NaI} + U_{KCl}$ and $U_{NaCl} + U_{KI}$ are almost equal, and their difference would be considerably influenced by inaccuracies in the values of U. If Q be calculated from the heats of formation of the individual crystals, as was first attempted by the author,[9] very inaccurate results are also obtained. Fajans[10] has increased the accuracy of estimating Q by calculating it in an indirect way from the heats of solution which can be accurately determined. He assumed the interaction of NaCl and KI to NaI and KCl to take place as follows:

First, the salts NaCl and KI are dissolved in a large volume of water, whereby $L_{NaCl} + L_{KI}$, the heat of the solution per mol, is liberated. In the solution the salts are completely dissociated, and the ions aN^+, K^+, Cl^-, and I^- are absolutely free. Hence the dissolution of the two salts KCl and NaI would give exactly the same solution, the heat $L_{KCl} + L_{NaI}$

being liberated. If the ions be removed from the solution and built up to form the crystals KCl and NaI, the energy $-(L_{KCl} + L_{NaI})$ must be supplied. In changing the one pair of salts to the other by this method of solution, the total heat

$$Q = L_{NaCl} + L_{KI} - L_{KCl} - L_{NaI} \quad . \quad . \quad (17)$$

is evolved. From this formula (17) Fajans has calculated Q from the known heats of solution, and compared them with the theoretical values (16) from the lattice theory. The following table shows his results:

TABLE I

Reaction.	Q from the lattice theory.	Q from the heats of solution.
KCl + LiBr = KBr + LiCl	4	3·6
KCl + LiI = KI + LiCl	7	7·2
KCl + NaBr = KBr + NaCl	3	2·0
KCl + NaI = KI + NaCl	5	3·4

The results justify the further development of the theory.

6. The Ionisation-energy of Positive Ions

It will be necessary, however, to investigate not only the *combination* of ions, but also the mechanism of their *formation*. The theory of the process of splitting off electrons—the formation of positive ions—is at about the same stage of development as the above theory of the combination of ions. For the latter, the heat of combination U could not be obtained solely from the properties of the atoms or ions, but use had to be made of measurements of density and compressibility. Similarly, the work of separation of an electron from an atom cannot be deduced, except in a few instances, by simple calculation from its constitution, but it can be reduced to optical measurements admitting of

a high degree of accuracy. This fundamental connection was brought out by the investigations of Franck and Hertz,[11] and depends on the ideas concerning the constitution of atoms evolved by Bohr.[12]

It is well known that the line spectra of the elements can be arranged in series the frequencies in which obey laws of the following form :

$$\nu_n = \nu_\infty - f(n) \quad . \quad . \quad . \quad (18)$$

where n is the number of the series line, and $f(n)$ is a function which approaches zero as n increases. The lines of the series, therefore, crowd towards the " series-limit," ν_∞. For the well-known Balmer series for hydrogen,

$$\nu_n = \nu_\infty - \frac{K}{n^2} \quad . \quad . \quad . \quad (19)$$

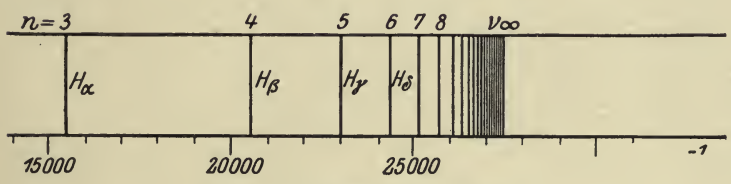


FIG. 5.—Hydrogen series (Balmer).

where the so-called Rydberg constant,

$$K = 3{\cdot}291 \times 10^{15} \text{ sec.}^{-1}, \text{ and } \nu_\infty = \frac{K}{4}.$$

Fig. 5 shows this series ; it will be observed that the lines in the ultra-violet come closer and closer together, and crowd up at the series-limit ν_∞.

This regularity is interpreted by Bohr as follows : As in classical electro-dynamics, he assumes that the exchange of energy between the atom and the light radiation is effected by an electron which we will call the " optical electron." But contrary to all teachings of the classical theory, the atom is assumed to possess a series of " stationary " states,

in which the electron revolves in definite orbits without radiating energy. The energy-contents of these states differ by finite amounts; they are best measured by the work W necessary to detach the optical electron from the atom, and to bring it to rest at an infinite distance. If the energy of the atom in this "ionised condition" be taken as zero, in another stationary state it will be equal to $-W$. As already mentioned, the atom is assumed to radiate no energy when in a stationary condition, but when it goes from one of these stationary conditions Z' to another, Z, a radiation—absorption or emission—is assumed to occur, according as the expenditure of energy $W' - W$ is positive or negative.

Bohr naturally cannot allow the rules of classical electrodynamics to hold for the law of this radiation. Instead, he uses Planck's quantum theory,[13]* according to which the frequency ν of a radiation and its energy, E, are related by the equation

$$h\nu = E \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where h is the universal constant discovered by Planck, the value of which is

$$h = 6{\cdot}54 \times 10^{-27} \text{ ergs/sec.} \quad . \quad . \quad (21)$$

Accordingly, Bohr states that the transition from the condition Z', with work of separation W', to the condition Z, with work W is, if W is greater than W', accompanied by an emission of a frequency ν, according to the equation

$$h\nu = W - W' \quad . \quad . \quad . \quad (22)$$

and that the reverse transition can only be produced by the absorption of a radiation of frequency ν. If one gives to Z' a series of values Z_1, Z_2 . . . and allows the system to go from these conditions to one and the same final condition Z,

* A survey of Planck's quantum theory will be found in "Naturw.," 6, part 17, pp. 195-263 (1918).

the energy of which must obviously be smaller than that of any of the starting conditions (and hence W must be greater than any one of W_n), one obtains the frequencies

$$\nu = \frac{1}{h}(W - W_n) \quad . \quad . \quad . \quad (23)$$

and this equation becomes identical with the series-law (18) if one inserts

$$W = h\nu_\infty, \; W_n = hf(n) \quad . \quad . \quad (24)$$

Hence the terms of the series-formula, multiplied by Planck's constant h, give directly the separation-energies of the electron in each of the individual stationary states.

In particular, the work of separation for the limit-orbit of the optical electron depends on the series-limit ν_∞ ; to this orbit the electron returns after the emission of all the lines of a series. The limit-orbit can be any one of the stationary orbits of the atom ; for each such orbit one obtains another line-series with another limit. The occurrence of these series depends on the conditions of excitation, and varies in flames, in Geissler tubes, and in sparks. For an orbit to occur frequently as a limit, it must be so arranged that a considerable portion of the atom is in that state in which the electron travels in this orbit. This is achieved by supplying energy from outside by electrical discharges, increase in temperature, or by the absorption of light.

But when there is no addition of energy the optical electron is in the orbit corresponding to the normal, unexcited state of the atom. If it absorbs energy in this condition, there is formed a series, the limit of which, ν_∞, multiplied by h, gives the energy of separation of the electron from the unexcited atom. Now this is the work of ionisation, and a fundamental connection has been established.

The work of ionisation is obtained from the equation

$$J = h\nu_\infty \quad . \quad . \quad . \quad . \quad (25)$$

where ν_∞ is the limit of the frequency series which the atom absorbs in its natural unexcited condition.

This law has been amply confirmed by the work of Franck and Hertz and their collaborators.[11] The work of ionisation is measured directly thus: A stream of electrons of definite velocity is directed into the gas, and the number passing through the layer of gas and their emerging velocity are determined. If the gas is electro-positive (rare gases, vapours of metals), the collisions of the electrons with the atoms proceed elastically as long as the electron-velocity does not reach the definite limit given by its kinetic energy becoming equal to the difference

$$W - W_1 = h\nu_1,$$

which is the energy which must be supplied for the first line of the absorption-series. As soon as the electrons have attained this energy they give it up on collision with the atoms, which in turn lose it again as light radiation. This was first confirmed by Franck and Hertz for the mercury line 2536Å.[14] Similarly, but less conclusively, the quantities of energy necessary for the other series-lines have been investigated, and Franck and Einsporn have succeeded in determining a large number of lines in mercury vapour by means of the energy lost by the bombarding electrons.[15] Lines are also obtained which may be calculated from the series-formulæ, but which are not available to optical methods. Now the loss of energy by the bombarding electrons clearly occurs at that velocity required for the complete ionisation of the atom. This energy of ionisation is measured by the electrical tension in volts through which the electron must pass, in order to attain the final velocity necessary for ionisation. The ionisation-tensions for many elements have been measured by this method of electron-shock, and the law (25) has been verified for all. As the series-limits are known with great accuracy—far greater

than that obtainable electrically—one has an accurate optical measure of the work of ionisation of electro-positive elements. The following table gives for the alkali metals the frequencies ν_∞, together with the ionisation-energies J (in kg.-cals. per mol), calculated from them:

TABLE II

Element.	ν_∞.	J.
Li	43484	123·0
Na	41445	117·0
K	35006	99·0
Rb	33685	95·1
Cs	31407	88·6

The values J, like the lattice-energies U, are established and fundamental thermo-chemical constants. We will now consider chemical reactions, the heats of reaction of which are determined solely by these two quantities U and J. Such a reaction is

$$NaCl + K = KCl + Na \quad . \quad . \quad (26)$$

where the metals K and Na are in the gaseous state. The heat of reaction is obviously

$$Q = U_{KCl} - U_{NaCl} + J_{Na} - J_K \quad . \quad . \quad (27)$$

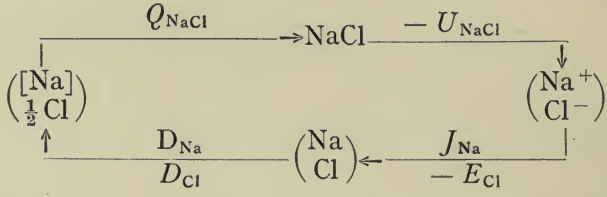
Again, Q can be determined from the known heats of the reactions between the solid metals and the salts and the heats of vaporisation of the metals. Hence the theory can be tested.[9]

7. The Electron-affinity of Electro-negative Atoms

We can also arrive at the same result by another method which, at the same time, involves the third fundamental of thermo-chemistry—the energy accompanying the formation

of the negative ions. From numerous chemical facts systematically arranged by Kossel,[6] one can deduce that the process of attaching an electron to the atom of an electronegative element—a halogen atom, for instance—is accompanied by the production of energy. The negative ion is therefore more stable than the neutral atom, which has an affinity for an electron. As a measure of the electron-affinity we take the work E, necessary to detach an electron from the ion and bring it to rest at an infinite distance.

The relation between E and the above-mentioned energies will be clear from the following diagram :



(28)

if we imagine 1 mol of solid NaCl dissociated into the free ions Na^+ and Cl^-, and these converted into the neutral atoms Na and Cl by the exchange of electrons, and then the Na vapour condensed to solid [Na], and every 2 Cl atoms combined to a $\frac{1}{2}$ mol of Cl_2 molecules. From this we can return to the NaCl, at the same time obtaining the heat of reaction Q_{NaCl}. In each change the heat liberated is measured. Apart from the already defined symbols, the following additional are used : D_{Na} for the heat of vaporisation of the metal, and D_{Cl} for the heat of dissociation of a $\frac{1}{2}$ mol of Cl_2 gas into 1 mol of Cl atoms. From the above cycle it can be seen that

$$Q_{NaCl} - U_{NaCl} + J_{Na} - E_{Cl} + D_{Na} + D_{Cl} = 0 \qquad (29)$$

Here every term is known except E_{Cl} ; it can, therefore, be calculated from the values of the others. If, instead of NaCl, we take other alkali chlorides, several independent values for E_{Cl} are obtained ; these, apart from errors in the

measurement of the other terms, should be equal. Calculation has shown that this is, indeed, so, and therein lies a confirmation of the theory. In this manner Born (1919) calculated the electron-affinities of the halogens [21]; the value of E_{Cl} then found, however, was much too high, a later determination of the heat of dissociation of chlorine gas by von Wartenberg [16] and his pupils has shown that this value is only about half that previously accepted ($D_{Cl} = 55$ kg.-cals., not 106). Based on the most reliable data we now have

$$E_{Cl} = 86\,;\ E_{Br} = 86\,;\quad E_{I} = 79 \text{ kg.-cals.} \quad . \quad (30)$$

In these figures the slight decrease with increasing atomic weight appears questionable; it is probable that they will undergo still further and considerable alterations with fresh determinations of the thermo-chemical data.

Franck [17] has recently indicated a direct method for the determination of the electron-affinities of the electronegative elements; it is based on the following consideration. When an electron approaches an atom it rushes towards it, releasing a certain quantity of energy W, which can have varying values since the electron can have different initial velocities, and consequently different amounts of kinetic energy. The smallest value for W, corresponding to the electron being originally at rest relatively to the atom is obviously the electron-affinity, E. Each value for W is related by Bohr's quantum-law $W = h\nu$ to a frequency ν; these frequencies form a continuous spectrum which ends at the frequency ν_0, where $h\nu_0 = E$. In a photograph of the iodine spectrum by Steubing,[18] Franck has found such a spectrum which even with the greatest dispersion could not be resolved into bands, but remained continuous; further, with rising temperature it became more distinct, whereas the band spectrum originating from the iodine molecules and photographed at the same time became

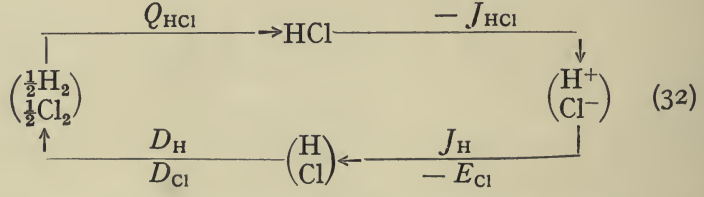
weaker. It is therefore highly probable that this spectrum originates from the iodine atoms. A similar continuous spectrum for bromine was found in photographs by Eder and Valenta;[19] for chlorine it was recently discovered by Angerer.[20] From the photographs the following values are obtained:

$$E_{Cl} = 89{\cdot}3\,;\ E_{Br} = 67{\cdot}5\,;\ E_{I} = 59{\cdot}2 \text{ kg.-cals.}\,; \quad . \quad (31)$$

of these the first agrees well with the lattice theory value: the discrepancies among the others are probably due to the inaccuracy of the thermo-chemical data used in calculating the lattice theory figures.

8. The Ionisation-energy of the Hydrogen Halides

Finally, we return to the problem of the gaseous hydrogen halides, which formed the starting-point of our considerations of the combination-energies of the ions.[21] We have now all the data with which to determine them. The energy set free by the union of 1 mol of H^+ ions with 1 mol of Cl^- ions to form HCl molecules, we will call J_{HCl}. Then we have the following cycle:



(32)

This needs no description. But something must be said about the ionisation-energy J_H of the H atom, for this cannot be obtained by direct measurement, but must be calculated from Bohr's theory. The H atom is one of the few for which Bohr's theory completely explains the orbit of the optical electron, for this electron is the only one that revolves completely round its positive atom-nucleus; it moves under the influence of the Coulomb attraction of the nucleus in

circles or ellipses, like the planets round the sun, and in accordance with the same Kepler laws. However, here all Kepler ellipses are not possible, but an equation, deduced from Planck's quantum theory, defines a definite series of orbits which are the " stationary states " of the atom. The energy of the nth orbit is

$$W_n = \frac{Kh}{n^2} \quad . \quad . \quad . \quad (33)$$

where K is the Rydberg and h the Planck constant. Consequently the series given by

$$\nu_\infty = K\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad (34)$$

is possible. Its limits have the frequencies

$$\nu_\infty = \frac{K}{m^2} \quad . \quad . \quad . \quad . \quad (35)$$

Among these is the above-mentioned Balmer series (19), for which $m = 2$, in the emission of which series the electron therefore jumps from the nth orbit back to the second.

The first orbit corresponds to the unexcited condition of the H atom, for which $\nu_\infty = K$, and therefore the work of ionisation $J = hK$. From this the ionisation-energy of 1 mol of H atoms is found to be

$$J_H = NhK = 310 \text{ kg.-cals.} \quad . \quad . \quad (36)$$

It is this number that is used in the cycle (32), which now yields an equation analogous with (20).

$$Q_{HCl} - J_{HCl} + J_H - E_{Cl} + D_H + D_{Cl} = 0 \quad . \quad (37)$$

In this the value obtained from (29) can be inserted for $D_{Cl} - E_{Cl}$ with the following result:

$$Q_{HCl} - J_{HCl} + J_H + D_H + U_{NaCl} - Q_{NaCl} - J_{Na} - D_{Na} = 0 \quad (38)$$

In this equation all the quantities are known except J_{HCl}; this, then, can be calculated, and the same value should

always be obtained whichever univalent metal, say K or Rb, instead of Na, be used: herein lies the proof of the theory. Born made this calculation in 1919 and actually found, for the work of ionisation of hydrogen halides, definite values, almost independent of the metal used:

$$J_{HCl} = 322\ ;\ J_{HBr} = 308\ ;\ J_{HI} = 299 \text{ (kg.-cals.)} \quad (39)$$

It is remarkable that these values are not only nearly equal, but also approximate, to the ionisation-tension of the H atom, for which, using Bohr's theory, we have just found the value $J_H = 310$ kg.-cals. (36). The separation of a negative ion, such as Cl^-, Br^-, or I^-, from the H^+ ion therefore yields almost the same amount of energy as does the removal of an electron from the H^- ion. Haber [22] first drew attention to the importance of this relation to the study of the structure of the atom.

The values given in (39) can be tested by direct measurement, since the hydrogen halide molecules can be dissociated into their ions by the electron shock method, just as a metal atom can be divided into its ion and an electron. These experiments were made by Knipping; [23] to the figures he has found, a correction must still be applied. As it is difficult to measure directly the tension-gradient through which the bombarding electrons pass, he mixed helium with the gases under investigation and used it as a standard. In this way the absolute measurement of the ionisation-tension of helium, by Franck and Knipping's method, was combined with the electron shock method; in the meantime, however, Lyman [24] succeeded in determining spectographically the ultra-violet principal series of helium, and from these observations Franck [25] was able to deduce the ionisation-tension with the great accuracy of optical measurements, and found it to be about 18 kg.-cals. The corrected Knipping figures [39] are:

$$J_{HCl} = 313\ ;\ J_{HBr} = 299\ :\ J_{HI} = 290 \text{ kg.-cals.} \quad (40)$$

The value for HCl has also been determined by Foote and Mohler,[26] who found $J_{HCl} = 323$. The agreement with the figures calculated from the lattice theory is very satisfactory.

If, conversely, the Knipping figures (40) are taken as correct, then with the aid of (38) the lattice-energies can be expressed completely by quantities capable of direct measurement, excluding that is J_H which has been definitely established from theory. Hence all the quantities occurring are comparatively certain, excepting the heat of dissociation of hydrogen D_H, for which estimates vary between 35 and 50 kg.-cals. Taking the probable value $D_H = 40$ kg.-cals., the following table is obtained. In this the lattice-energies (U_{calc}) calculated according to (14) are placed beside the values deduced according to (38) from measurable quantities (U_{obs}). The caesium salts are omitted, because the lattice structure found in CsCl is not of the normal type illustrated in Fig. 4. The lithium salts are missing; owing to the minuteness of the Li ion the exponent n of the law of repulsion (8) is presumably much less than 9.

	U_{obs}	U_{calc}		U_{obs}	U_{calc}		U_{obs}	U_{calc}
NaCl	183	182	KCl	165	162	RbCl	161	155
NaBr	170	171	KBr	154	155	RbBr	151	148
NaI	159	158	KI	144	144	RbI	141	138

The agreement is so striking that the foundation of the electrostatic theory of the molecular forces may be regarded as proved.

Taking, for the lattice-energies, the theoretical values (U_{calc}), and, for the work of ionisation of the hydrogen halides, the observed figures (40), then from the equation (38) the heats of formation Q of the hydrogen halides can be calculated. This means determining theoretically, for the

first time, that fundamental chemical quantity—the heat of reaction of a gas reaction at absolute zero. This is the first advance into what we have indicated as the fourth stage of physical chemistry.

9. The Heat of Vaporisation of Monovalent Metals

We must now mention some very interesting work by Haber,[27] who has calculated from the lattice-energy the energy of a typical homopolar process, the heat of vaporisation D of monovalent metals. He assumes the solid metal to be composed of positive metal ions and electrons, just as salts of the type NaCl comprise positive metal ions and negative halogen ions. Then the process of vaporisation can be divided into two: First, the heteropolar reaction, involving the dissociation of the lattice into positive ions and electrons; and then the reunion of these to form neutral metal ions. We can, therefore, write

$$D = U - J$$

where U is the lattice-energy and J the ionisation-tension of the metal. To calculate U, the exponent of repulsion n must be known; this is obtained, as with salts, from the compressibility. Here, however, n does not always equal 9, but assumes various values—for the alkalies, between 2·5 and 3·4; for copper, 8·0; for silver, 9·0. The heats of vaporisation D are obtained by subtracting J from the energies U calculated from these n-values; they agree remarkably well with observed values.

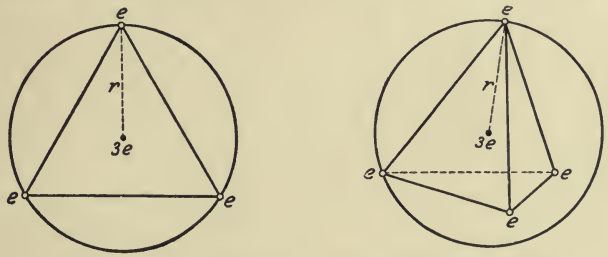
Even if objection can be made to Haber's hypothesis of the structure of metals, it would still seem to be fundamentally true.

Conclusion

This theory is also being extended in other directions. Thus Fajans [28] is endeavouring by its aid to obtain more

accurate knowledge of the size, energy, and mobility of the ions in aqueous solutions.

From the physical side, the electrostatic conception of the lattice-energy U is supported by the fact that other physical properties of the crystals have been calculated from the same assumptions concerning atomic forces. Here also the author has obtained good agreements in some cases,[29] and, in others, distinct indications as to how the theory may be improved.[30] Apart from the crystals of the alkali halides, fluorspar (CaF_2), zinc-blende (ZnS), galena (PbS), periclase (MgO), and calcium oxide (CaO) have been closely investigated.[31] The results obtained are important in the thermochemistry of divalent elements. Thus it can be shown,[32]



FIGS. 6 and 7.—Illustrating the idea of electron-affinity.

that the affinity of the divalent sulphur atom for its two electrons is $E_s = 45$ kg.-cals. ; for oxygen, no data of sufficient accuracy for the determination of its electron-affinity are available.[31] The determination of the electron-affinities of the halogen atoms is of the greatest importance in the solution of the problem of the structure of atoms. At first glance it seems impossible to construct from purely electrical forces an atom which, in the neutral state, is less stable than after it has taken up an electron. But Kossel [6]—admittedly in another connection—has shown that this is conceivable. To give an example, let us take as a crude diagram of the atom a rigid sphere, having a radius r, and a positive charge $3e$. If we add to it electrons, assumed to

be points, they will attach themselves in regular figures to the surface of the sphere. Three electrons, added to the neutral atom, form an equilateral triangle (Fig. 6), four electrons, added to the negative monovalent ion, form a regular tetrahedron (Fig. 7). Now we can readily obtain from these figures the following expressions for the electrostatic energies of these two configurations:

$$\phi_3 = -\frac{e^2}{r}(9 - \sqrt{3}) = -\frac{e^2}{r} \times 7{\cdot}269,$$

$$\phi_4 = -\frac{e^2}{r}\left(12 - \frac{3\sqrt{3}}{\sqrt{2}}\right) = -\frac{e^2}{r} \times 9{\cdot}326.$$

Therefore ϕ_4 is less than ϕ_3, i.e. the ion is more stable than the neutral atom.

Naturally, this model has no claim to represent reality, but it illustrates clearly the idea of electron-affinity. Nevertheless, it is to Bohr's theory of the atom that we must look for the complete solution of the problem.

When we contemplate the path by which we have come we realise that we have not penetrated far into the vast territory of chemistry; yet we have travelled far enough to see before us in the distance the passes which must be traversed before physics can impose her laws upon her sister science.

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